FINAL QUALITY ASSURANCE PROJECT PLAN

for

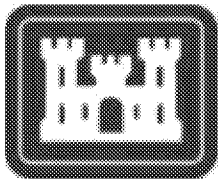
PASSIVE SAMPLING

at

River Operable Unit, Bradford Island
CASCADE LOCKS, OREGON

Prepared by

U.S. ARMY CORPS OF ENGINEERS
Portland and Seattle Districts



January 23, 2020

This page left blank for double-sided printing.

TITLE AND APPROVAL SHEET
QUALITY ASSURANCE PROJECT PLAN (QAPP)
PASSIVE SAMPLING
RIVER OU, BRADFORD ISLAND, CASCADE LOCKS, OREGON

This Quality Assurance Project Plan (QAPP) describes sampling activities and Data Quality Objectives (DQOs) for passive sampling at the River OU, Bradford Island, Cascade Locks, OR. The QAPP is based on the *Intergovernmental Data Quality Task Force Uniform Federal Policy for Quality Assurance Project Plans Guidance (EPA 2009).*

BUDAI.CHRISTINE.M.1231369259 Digitally signed by BUDAI.CHRISTINE.M.1231369259 Date: 2020.01.17 18:24:40 -08'00'

Chris Budai, Project Manager, NWP — Date

William Gardiner, Study Technical Lead, NWS — 1/22/20 Date

SUESS.ALISON.M.1512196469 Digitally signed by SUESS.ALISON.M.1512196469 Date: 2020.01.14 13:02:51 -08'00'

Alison M. Suess, Ph.D., Chemist, NWS — 1/14/2020 Date

This page left blank for double-sided printing.

TABLE OF CONTENTS

APPENDICIES

LIST OF ACRONYMS

µg/L	microgram per liter
AOPC	area of potential concern
$CaCO_3$	calcium carbonate
CCB	continuing calibration blank
CCV	continuing calibration verification
CoC	chain of custody
COPC	contaminant of potential concern
CPR	cardiopulmonary resuscitation
DoD ELAP	Department of Defense Environmental Laboratory Accreditation
DoD QSM	Department of Defense Quality Systems Manual
DMC	deuterated monitoring compounds
EDD	electronic data deliverables
EDTA	ethylenediaminetetraacetic acid
EPA	United States Environmental Protection Agency
GC-MS	gas chromatography mass spectroscopy
HAZWOPER	Hazardous Waste Operations and Emergency Response
HDPE	high density polyethylene
HNO_3	nitric acid
HPAH	high-molecular-weight polycyclic aromatic hydrocarbon
ICB	initial calibration blank
ICV	initial calibration verification
JHA	Job Hazard Analysis
LCS	laboratory control sample
LOD	limit of detection
LOQ	limit of quantitation
mg/kg	milligram per kilogram
MS	matrix spike
MSD	matrix spike duplicate
ODEQ	Oregon Department of Environmental Quality
OU	Operable Unit
PCB	polychlorinated biphenyl
PDT	Project Delivery Team
POC	point of contact
PM	Project Manager
PQO	Project Quality Objectives
QC	quality control
RI	Remedial Investigation
RL	reporting level
SLV	screening level value
SOP	Standard Operating Procedure
TAG	Technical Advisory Group
UCL	upper confidence limit
UPL	upper prediction limit
USACE	United States Army Corps of Engineers
UFP-QAPP	Uniform Federal Policy Quality Assurance Project Plan
WP-QAPP	Work Plan with Quality Assurance Project Plan

1. PROJECT MANAGEMENT AND OBJECTIVES

1.1. Project Organization, Responsibilities and Authority

The Project Delivery Team (PDT) for this Work Plan (WP) includes members from USACE Portland and Seattle Districts.

The project team provides the overall framework for the data collection approach by defining project objectives and data quality requirements, and ensuring that they are met during the execution of the project. Project updates will be shared with the Technical Advisory Group (TAG) who will be coordinated with during development and provided final copies of the WP and QAPP by the USACE Project Manager (USACE PM). This section further describes the team project roles. Figure 1 and Table 1 present the project organization.

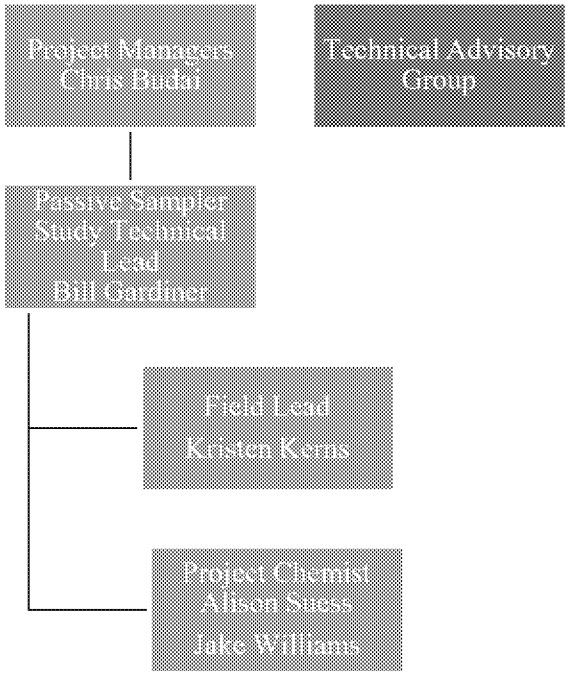


Figure 1. Project Organization Chart

Table 1. Project Organization and Distribution List

Personnel	Contact Information	Title
USACE		
Chris Budai	333 SW 1st Ave Portland, OR 97204 Phone: 503-808-4725 Email: christine.m.budai@usace.army.mil	Project Manager
William Gardiner	4735 E. Marginal Way S Seattle, WA 98134 phone: 206-764-3322 william.gardiner@usace.army.mil	Study Technical Lead
Alison M. Suess, Ph.D.	4735 E. Marginal Way S Seattle, WA 98134 phone: 206-764-3264 alison.m.suess@usace.army.mil	Project Chemist
Kristen Kerns	4735 E. Marginal Way S Seattle, WA 98134 phone: 206-764-3474 kristen.kerns@usace.army.mil	Field Lead

1.1.1. Communication Pathways

Communication is a key to the success of this project. Communication pathways describe the points of contact for resolving sampling and analysis problems, for distributing data to users, soliciting concurrence and obtaining approval between project personnel and contractors. Table 2 summarizes the communication pathways.

Table 2. Communication Pathways

Communication Driver	Responsible Entity	Name Phone Number	Procedure (timing, pathway, etc.)
USACE management for this project Overall direction and Point of Contact for public	Project Manager	Chris Budai 503-808-4725	Assures that the overall direction of the project is consistent with USACE guidance Liaison with the Public
QAPP approval	Technical Lead	Bill Gardiner 206-764-3322	Coordinates with Project Manager, Project Lead, Chemist and Field Lead on project technical issues
Schedule, budget and technical issues			Reports to USACE PM regarding schedule, budget, and technical issues
Changes to schedule and budget			Notifies USACE PM of significant changes in execution or schedule
Oversight of final report Provides coordination among team members			Oversee USACE writing of final report and distribution to reviewers Provides input to QAPP and data reports

Communication Driver	Responsible Entity	Name Phone Number	Procedure (timing, pathway, etc.)
Writes QAPP with input from technical team members. Laboratory and data validation	Project Chemist	Alison M. Suess, Ph.D. 206-764-3264 Jake Williams 206-316-3157	Oversees writing of QAPP and Activity Hazard Analysis (AHA) and ensures revision approval within agreed timeframe Oversees laboratory work Writes data validation report Provides laboratory and data validation components of QAPP
Provide direction to field teams on sample collections Delivery of samples to laboratory Sampling activities summary Ensures compliance with Site Safety Health Plan (SSHP) AHA	Field Lead	Kristen Kerns 206-764-3474	Daily communication with team members during sampling events Coordinates with Project Chemist and laboratory for sample delivery Documents all field activities in Final Monitoring Report Briefs field team on SSHP and JHA and documents noncompliance Coordinates with Project Chemist

1.1.2. USACE Personnel Responsibilities and Qualifications

USACE Project Manager

The project manager (PM), Chris Budai, is responsible for the execution of the scope, schedule, and budget for the Bradford Island CERCLA project. She is the primary POCs for communications with stakeholders. The USACE PM also has the authority stop work of USACE staff. The USACE PM is the primary document controller for the WP.

USACE Technical Lead

The Technical Lead, Bill Gardiner, will oversee all activities of the USACE project delivery team (PDT), including quality assurance reviews, and maintain regular coordination to ensure adequate and timely flow of information for all work.

USACE Project Chemist

The Project Chemists, Alison M. Suess, Ph.D. and Jake Willams, are directly responsible for laboratory coordination and matters related to chemistry. They are responsible for providing additional guidance to the Field Sampling Lead (Kristen Kerns) in any matters relating to project chemistry and data quality.

Field Sampling Lead/Site Health and Safety Officer

Kristen Kerns is the designated field sampling lead and site safety and health officer (SSHO) for this effort. She is responsible for coordinating the sampling with relevant Bonneville Project staff, execution of sampling, and shipping of samples to the project laboratories. She may communicate directly with the PM, Technical Lead, and Project Chemists as needed during the field sampling event.

Special Training Requirements and Certifications

Project staff shall be qualified to perform their assigned jobs. Field sampling personnel conducting or monitoring sampling activities are to be trained by the field sampling lead in accordance with established USACE protocols.

Field Staff

All project staff participating in on-site field activities shall have current HAZWOPER training in accordance with 29 Code of Federal Regulations (CFR) Part 1910.120. The field sampling lead has HAZWOPER training in accordance with the same standard as well as a current certification in first aid and CPR.

Laboratory Contact

The analytical laboratories and applicable information that will be used for this project are listed below in Table 3.

Table 3. Analytical Laboratory and Contacts

Lab Name	Lab Address	POC	Contact Info	Role
Texas Technical Institute	2500 Broadway Lubbock, TX 79409-0000	Dr. Danny Reible	806-834-8050 Danny.Reible@ttu.edu	Technical Lead
		Alex Smith	Alex.V.Smith@ttu.edu	Graduate Student

1.1.3. Technical Advisory Group Personnel Responsibilities

Technical Advisory Group members represent their respective agencies and provide technical review of the QAPP.

1.2. Data Quality Objectives and Measurement Performance Criteria

1.2.1. Development of Data Quality Objectives Using the Systematic Planning Process

As described in the Final Work Plan (USACE, 2019), the goal of this study is to support remedial design in the River OU by identifying areas along the northern shoreline of Bradford Island that may still be serving as a primary source of PCB contamination to fish and other aquatic receptors and to identify those areas that may not be an ongoing source of PCBs. Measuring concentrations of PCBs in water at the sediment-water interface (porewater and near-bottom water) will be used to identify source areas.

The two primary goals of this study are:

1) Identify locations along the northern and eastern tip of Bradford Island that are potential source areas.

2) Use passive sampling results as a line of evidence to eliminate source areas along the northern and eastern tip of Bradford Island.

To support these overall goals, Data Quality Objectives (DQOs) were developed through the systematic planning process as described in the UFP-QAPP Guidance. This section presents the DQOs for the passive sampler program. The DQO process defines criteria that will be used to establish the final data collection design (U.S. EPA 2006). Based on the study goals listed above, the DQOs were developed to support the selection of sampling and analysis methods and an overall study design that leads to data appropriate to answer the study questions. The DQOs developed for the passive sampler study, the data types, and the analytical approaches are presented in the following subsections and are summarized on Table 4. Specific performance goals, referred to as Data Quality Indicators, for the individual analytical methods are discussed in Section 3.0 after the methods have been introduced.

DQO-1: Identify locations that are ongoing sources of PCBs at Bradford Island. The first DQO is to determine whether there are ongoing source areas present in the River OU north and east of Bradford Island. This first DQO establishes individual locations or localized areas that are acting as a source of PCBs to the sediment and biota of Bradford Island. Source areas are those locations with concentrations of total PCBs that are highly concentrated, highly mobile, or not reliably containable. In general, PCBs associated with the legacy waste that may still be present in the River OU are unlikely to be highly mobile; however, they may be "highly concentrated" and "not reliably containable".

Investigative methods to determine whether there are locations that have PCBs that are highly concentrated or not reliably contained will include measurement of freely dissolved PCBs in water at the sediment-water interface (the porewater and near-bottom water). PCB congeners will be measured using passive samplers that are placed in situ for a minimum of 28 days. A total of 163 low-density polyethylene (LDPE) passive samplers will be deployed at a high density across the study area. Individual locations or groups of locations that have PCB concentrations that are elevated relative to the surrounding area will be considered source areas in the remedial design.

Source areas will be identified for total PCBs (based on the sum of 46 selected congeners) based on several types of analysis: 1) points identified using Grubb's outlier test and/or Q-Q plots to help graphically illustrate potential outliers and population partitioning methods to evaluate whether distinctly separate groups of congeners are present; and/or 2) points fitting the definition of source material (10 times the 90UCL); and/or 3) groups of stations identified as significantly elevated through geostatistical analysis (kriging).

DQO-2: Identify locations that may not be ongoing sources of PCBs at Bradford Island. The second DQO is to determine areas that are not sources in the River OU north and east of Bradford Island. This second DQO establishes individual locations or localized areas that *may not* be acting as a source of PCBs to the sediment and biota of Bradford Island. This DQO allows remedial design to adjust remedy alternatives that are not targeted to source areas (areas that are highly contaminated or with PCBs that are not reliably contained).

Investigative methods to determine whether there are locations that may not be source areas are similar to those for DQO-1, with the exception that a negative result using passive samplers will be considered a first step, to be followed by sediment and biota sampling.

DQO-3: Identify locations that may represent an area of groundwater upwelling at Bradford Island. This final DQO is to determine the potential for groundwater upwelling along the northern and eastern portion of Bradford Island. To do this, time series graphs of temperature readings during deployment will be compared to time series graphs of surface water temperature readings collected at the same time. Significant differences in temperature between surface water and individual sediment water interface may be indicative of groundwater upwelling. This may ultimately aid in the interpretation of PCB results obtained through collocated passive sampling.

Table 4. Data Quality Objectives

DQO Step	DQO 1	DQO 2	DQO 3
1. State the problem	PCB concentrations in Bradford Island biota and sediment remain elevated following sediment removal in 2007 suggesting the potential for an ongoing source to the River OU. In order to complete the remedial design for the River OU, locations that may be acting as a source, as well as those areas that are not acting as a source, need to be identified. However, the complex bottom topography and lack of bedded sediment do not support the use of conventional sediment sampling methods to identify sources.		It is unknown whether groundwater upwelling may have an influence on PCB concentrations measured using passive sampling.
2. Identify the goals of the study	Identify locations that ARE ongoing sources of PCBs at Bradford Island	Identify locations that MAY NOT be ongoing sources of PCBs at Bradford Island	Identify groundwater upwelling locations
3. Identify the information inputs	Concentrations of PCB congeners at the sediment-water interface	Concentrations of PCB congeners at the sediment-water interface	Individual point samples of time series water temperature readings at the sediment-water interface and surface water
4. Define the boundaries of the study	Northern and eastern portions of Bradford Island – areas with legacy waste and previously observed elevated PCB levels as described in Section 2.1.3		
5. Develop the analytical approach	Outlier test (Grubb's Test); population partitioning	Outlier test (Grubb's Test); population partitioning	Analysis of difference between time series temperature results for sediment water interface at individual point samples with collocated passive samplers versus surface water.
	Ten times 90UCL (ProUCL)	Ten times 90UCL (ProUCL)	
	Geospatial analysis	Geospatial analysis	
6. Specify performance or acceptance criteria	Performance or acceptance criteria are described in Section 2, including field QC samples and laboratory QC samples. DQIs for laboratory analyses will be met, as described in Section 2		Individual temperature measurements at the sediment water interface and surface water samplers sufficient to develop a time series plot and calculate an average at each individual point sample with a recoverable collocated passive sampler.
7. Develop the detailed plan for obtaining data	LDPE passive samplers will be deployed on the sediment surface for 28 days at 163 sampling locations that have been selected based on a systematic sampling design with a triangular grid and a random start. Each sampler will be extracted and extracts analyzed for 46 PCB congeners. A full list of total quantifiable congeners will be measured in extracts from 10 samplers. Equilibrium concentrations will be calculated for each congener using performance reference compounds and results present by congener and as total PCB congeners based on the list of 45 congeners		Individual temperature sensors will be collocated with passive samplers during deployment. Five temperature sensors suspended mid water column will also be deployed. Temperature readings will be recorded at a minimum of every hour during the equilibration period then retrieved with the passive samplers at the end of equilibration. Temperature data will be downloaded from sensors and analyzed for any correlation with PCB concentrations measured in passive samplers.

1.2.2. Subset of PCB Congeners for Analysis

As discussed in the Final Work Plan, each individual PE sampler will be analyzed for a group of PCB congeners. To allow for an increased number of sampling locations, the congener list was refined to include those congeners that are significant contributors to the PCBs observed in Bradford Island media (sediment, tissues, porewater, stormwater) and those congeners that are significant contributors to Aroclor 1254, the primary aroclor present at the site. The list presented in the work plan was modified to incorporate coeluting congeners and a total of 46 congeners will be measured for each station. The final list of congeners for passive sampler analysis, as well as the basis for their inclusion, is presented in Table 5. Some of the congeners are currently noted as "TBA-to be added" to the current TTU method while others that exhibit coelution with other congeners are referenced as providing "SQ- Semi quantitative" analysis. Because of this coelution, it may not be possible to separate the congeners quantitatively, thus a semi-quantitative concentration will be reported.

A full scan of 130 congeners will be analyzed for a subset of 10 stations across the sample area. The 130 congeners represents the full list of congeners for which individual quantification has been developed. TTU analyzes a subset of the full 209 PCB congener list where they can positively separate the congeners to achieve an accurate quantification. To-date, TTU has not identified a need for attempting to quantify all 209 in environmental media. Two stations will be selected from each sampling subarea to evaluate the relative contribution of the 46 selected congeners to the totals. The stations identified for full congeners list are identified in Section 2.

Table 5. Subset of PCB Congeners for Analysis

PCB Congener	Common in Bradford Island Media	Component of Aroclor	Congener of Ecological Concern	Addition since work plan	In Method	To be added (TBA) or semi-quant. (SQ)	
6	●				●		
8	●		●		●		
11	●				●		
16	●				●		
18	●		●		●		
19	●				●		
44		●	●		●		
47			●		●		
49				●		TBA	
52	●	●	●		●		
61	●			●	●		
65			●		●		
70	●	●			●		
74	●				●		
76	●				●		
83	●				●		
86	●			●		TBA	
87	●	●			●		
90	●				●		
93	●				●		
95	●	●			●		
97	●	●				SQ	
98	●			●		TBA	
99	●	●			●		
100	●			●		TBA	
101	●	●	●		●		
102	●			●		TBA	
105	●	●	●		●		
108	●			●		SQ	
110	●	●			●		
113	●				●		
115	●				●		
118	●	●	●		●		
119	●				●		
125	●			●		SQ	
129	●					SQ	
138	●	●	●		●		
147	●			●	●		
149	●	●			●		
153	●	●	●		●		
160	●					SQ	
163	●	●			●		
168	●					SQ	
180	●		●		●		
187	●		●		●		
193	●			●	●		
				TOTALs	35	11	**46**

1.2.3. Statistical and Geospatial Analysis for Determination of Primary Source Material

As discussed in the Final Work Plan, a concentration threshold serves to identify those individual point locations that may indicate the presence of a primary source of PCBs.

In order to identify any individual points that may be indicative of a primary source, several statistical evaluations are being considered. One method being considered is to first evaluate the summed total subset of PCB congeners for each sample location and statistically evaluate the data using ProUCL Version 5.1 software. A 90% UCL could be calculated from the site wide data, and a multiplier of 10 could be applied to the 90%UCL to establish a point threshold. The basis for a multiplier of 10 is predicated on previous studies where sediments adjacent to areas with NAPL were found to have porewater concentrations ≥1,000 ng/L total PCBs. PCBs found in sediment porewater that were not associated with NAPL ranged in concentrations of 100 to 900 ng/L (Upal Ghosh, *personal communication*). This suggests that the presence of source material should result in concentrations at least an order of magnitude greater than non-source material for PCBs. Further, while Oregon DEQ guidance for establishing hot spot criteria is based on risk thresholds and point based evaluations, the application of a 10-times multiplier is used in hot spot threshold development, suggesting that concentrations of source material are an order of magnitude greater than materials that are not considered hot spots. Any individual points exceeding the established threshold could be considered as indicative of a primary source of PCBs.

In additional to evaluating the site on a sum total basis, the congener results will be evaluated in ProUCL for potential mixture populations. This may be warranted if distinctly different aroclor populations represented by a smaller subset of congeners dominate over others. Q-Q plots will be utilized to visually assess the data for the presence of mixture populations along with other statistical tools as warranted. If population partitioning methods become necessary, those distinct populations may be summed separately prior to calculating site wide 90% UCLs for those separate populations and applying a 10-times multiplier.

Analysis for outliers in the dataset will also be performed using ProUCL software to elucidate whether any other samples could be considered indicative of a primary source.

Another statistical method being considered for establishing threshold concentrations indicative of source material is to apply a multiplying factor (e.g. 2x, 3x, 4x) to the standard deviation of the site average concentration. This multiplication of the standard deviation would then be applied to the calculated site average. Similar to establishing a site wide 90%UCL and using a 10x multiplying factor, this evaluation would also be done on a point basis for each sample locations. Evaluating either by the summed total subset of PCB congeners or groups would be considered. Individual points that are greater than the site average plus a multiplying factor of the standard deviation could be indicative of points containing PCB source material.

Data will also be looked at holistically through geospatial analysis with Kriging the data. While the statistical analysis aims to identify potential PCB sources on an individual point basis, Kriging will help to provide analysis of PCB sources on a larger scale area basis. Kriging will be performed with ArcGIS,

or a similar software package. Kriging will be used to relate individual points to potential larger spatial trends in the data. The results of Kriging will be evaluated cooperatively with individual threshold exceedances to determine potential areas indicative of a primary source. Specific geospatial methods will continue to be developed prior to receipt of data and coordinated with the Technical Advisory Group.

All of the above proposed statistical and geospatial methods will continue to be coordinated with the Technical Advisory Group prior to receipt of the data and throughout the data evaluation process.

The methods used for statistical and geotechnical evaluation along with the results of this evaluation will be presented in the data evaluation report.

1.2.4. Temperature Monitoring to Assess Groundwater Influence

To help support interpretation of the passive sampling results, USACE will deploy temperature data loggers in conjunction with each individual passive sampler. Temperature will be recorded for the entire duration of deployment for each passive sampler. Identification of areas of groundwater discharge would allow the team to determine if groundwater discharging to the River (if it is) has an influence on results seen in the collocated passive samplers. Groundwater temperatures at the site are consistent (~9 - 13°C), but surface water (SW) varies from ~2 - 23°C. Differences in groundwater and surface water temperature at the groundwater /surface water interface may indicate discharge of groundwater to surface water.

1.2.5. Measurement Performance Criteria

Performance criteria specify the acceptable levels of uncertainty in measured data that can be used to support project decisions and achieve DQOs. Performance criteria for the analytical methods are specified in the laboratory procedures and are compliant with DoD QSM 5.1 unless otherwise noted. Any data which fall outside of these criteria must be justified, and the effects on decisions must be assessed.

1.3. Secondary Data Evaluation

No secondary data will be collected.

1.4. Project Overview and Schedule

Through project planning, the project team has agreed on the purpose of the project, the environmental questions that are being asked, and the environmental decisions that must be made. Project quality objectives have been developed specifying the type, quantity, and quality of data needed to ensure that project data can be used for the intended purpose to answer specific environmental questions, support environmental decisions, and determine technical activities that will be conducted. Table 6 provides a summary of the project tasks to be completed and Table 7describes the project schedule.

Table 6. Project Tasks

Plan, Prepare QAPP
• Prepare and finalize QAPP. • Test deployment method/apparatus
Sampling Tasks
• Deploy passive samplers and collocated temperature loggers • Retrieve passive samplers and collocated temperature loggers
Analytical Tasks
• Analyze LDPE for subset of congeners by GC-TQMS (Agilent 7890B) using SIM/SIM mode (EPA Method 1668c)
Quality Control Tasks
• Analytical methods QC will comply with DoD QSM or laboratory SOPs as applicable.
Secondary Data
• No secondary data will be collected.
Data Management Tasks
• USACE Seattle Project Chemist will review and store analytical data.
Documentation and Records
• Field notes will be recorded in a field notebook or on field log sampling sheets, then scanned and electronically stored. • Field notes will contain the following: date and time of sample collection, weather conditions, sample identification number, type of sample, any procedural steps taken that deviate from those outlined in this QAPP. • Laboratory analytical results will be stored.
Data Packages
• 100% of data packages will be validated through Stage 2A or similar by the USACE Seattle Project Chemist.
Data Review Tasks
• The laboratory performing analyses of samples will verify that all data are complete for samples received. • Data will be validated using the principles of the *USEPA Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review (2008).* • Validated data will be reviewed. • Data usability will be assessed. • Measurement performance criteria set in WP-QAPP checked. • Data limitations will be determined. Data compared to Project Objectives.

Table 7. Estimated Project Schedule

Task #:Description	Start	Finish
Task #1: Plan, Prepare QAPP, Field test		
Draft and Final QAPP	October 2019	December 2019
Field test deployment method/apparatus	November 2019	December 2019
Task #2: Field Work		
Sample deployment	January 2019	2 weeks after start date
Sample retrieval	February 2019 (Minimum 28 days after deployment)	2 weeks after start date
Task #3: Review Lab Data and Prepare Report		
Laboratory analysis	Initiate upon receipt of samplers	1 month after receipt of samplers
Receive/Review Data Report and store electronically	Upon completion of laboratory analysis	Upon completion of laboratory analysis
Draft Data Evaluation Report	Upon completion of laboratory analysis	60 days after completion of laboratory analysis
Final Data Evaluation Report	Upon receipt of TAG comments	30 days after receipt of TAG comments

2. DATA GENERATION AND ACQUISITION

2.1. Sampling Tasks

2.1.1. LDPE Sampling Apparatus

The sampling material for the passive samplers will be LDPE sheets (10 cm x 10 cm x 25 µm sheets) (or PE). This matrix is an established passive sampler material used for the measurement of PCBs in a variety of aquatic environments. The methods for both PE sheets and SPME samplers has been standardized (U.S. EPA, 2017) and a recent ESTCP project is currently working to refine the technology to improve the comparability of both field and laboratory methods across the industry. For the purposes of measuring PCB concentrations at the sediment-water interface, the PE samplers offer the advantages (over SPME samplers) of providing a higher surface to volume ratio at the sediment-water interface; they are durable for deployments in flowing water, and deployable in a variety of shapes and sizes. This allows the sampler apparatus to adapt to challenging environments while maximizing the amount of sampler exposed to the potential source areas.

Texas Tech University (TTU) will provide the PE sheets. Each sampler will be prepared with performance reference compounds (PRCs). PRCs are isotope labeled PCB analogues that are preloaded onto the PEs. The desorption rate constant of the PRCs will be used to approximate the absorption rate constant of the target analytes in order to quantify the equilibrium concentration.

A flexible, mesh envelope will secure the LDPE sheets. The mesh envelopes attach to the bottom of weighted pouches. The weighted pouch design ensures good contact between the PE sampler and the sediment surface and near bottom surface water, provides an anchor for the buoy lines, and allows for some interaction of the near-bottom water with the PE samplers. Weighted pouch construction includes

wire mesh with openings of a minimum of ½" to allow water movement. The weight will be enclosed in the wire mesh pouch and will consist of 10 pounds of 1.5 and 2" steel ball bearings. The weighted pouch has a buoy line attached.

2.1.2. Temperature Data Loggers

Temperature will be recorded hourly at a minimum during the approximate 30 day deployment using Hobo pendant temp/alarm 64K and associated Hoboware Pro V.3.X software. Temperature sensors will be individually identified with a location specific site ID. Deployment and retrieval times for each individual data logger will be recorded in field notes. Temperature sensors will be secured inside the weighted bag immediately adjacent to the polyethylene sheets. Upon retrieval, temperature data will be transferred from the sensors and hourly temperatures will be plotted for each individual sample location.

2.1.3. Sampler Deployment and Retrieval

Sampling Stations

In order to support the DQOs listed in Section 1.2.1, passive samplers will be deployed at a total of 163locations along the northern and eastern shoreline of Bradford Island (along with 5 passive samplers deployed mid water column). The sampling area was based physical and chemical characteristics described in the work plan and included the following:

- Known location of debris
- Location of outfalls
- Downstream of debris or outfalls
- Areas with elevated PCB concentrations in sediment or clams
- Bathymetry

Station locations within the sampling area were selected using Visual Sampling Plan® (version 7.0 PNNL 2014) software based on a systematic random sampling design with a triangular grid and random start. Stations were placed at a density such that the maximum distance between sampling points was 7 to 14 m. Additional modifications to the sampling design following finalization of the work plan include the removal of stations that were randomly located in locations unable to be sampled (e.g. upland points projecting in the sampling area) and the addition of sampling locations at the outer boundary of the sampling area to address TAG concerns to sample selected areas further offshore. Locations for the additional stations were based on the triangular grid established by VSP.

A table of all station locations with GPS coordinates for each location are presented in Appendix B. Figures of the sampling areas and selected stations is presented in Appendix C.

Deployment

Given the large number of samplers that need to be placed, along with the time and safety considerations associated with using a dive team for placement/retrieval, USACE will deploy and retrieve samples by boat and/or land (without divers).

Given the large number of samplers and duration required for deployment, LDPE samplers will be sent in batches to the field from TTU in order to minimize the time between sampler removal from the PRC loading solution and field deployment.

For boat deployment, the sampling vessel will maneuver to the pre-determined station coordinates using GPS. Because of the complexity of the river bed and the density of the stations, the sampling vessel will maneuver to each station using dynamic positioning. With dynamic positioning, the bow of the vessel would point into the current and work laterally across the sampling area. Alternatively, depending on field conditions, a three point anchor system may be used, with the vessel moving laterally across the sampling area using port and starboard anchors and moving upcurrent using the bow anchor. Once on station, the anchor lines will be tied off creating a stable sampling platform.

Once on station, each sampler – consisting of a passive sampler marked with the station number, temperature logger, and marker buoy marked with the station number, will be lowered to the bottom by hand using a deployment line. The deployment line will be an independent line that is weighted to decrease current influence and includes a triggered hook to allow release of the sampler and buoy line (See Appendix E for sampler schematics). Because the sampler needs to be placed in direct contact with the river bed and the river bed is uneven, the deployment line will be fitted with a real-time down-looking video camera to verify correct sampler placement and orientation on the sediment surface. Once the substrate has been considered suitable for deployment, the sampler will be released and station number, the time and date of sampler placement, coordinates recorded on a data sheet.

If the pre-determined station location is not suitable for sampler placement (e.g. based on visual observations of a boulder or large rocks), the sampler will be relocated to the nearest suitable location by moving laterally along the stern of the boat and along the port and starboard side of the boat (a search area of approximately 10 ft^2. If a suitable station cannot be located within the search area, the station will be abandoned and a contingency location will be selected from the prepared list of preselected alternatives. Both primary and secondary contingency locations have been identified (see appendices B and C). Primary contingency points will be selected first from the set of alternate locations.

Some sampling locations closest to the shoreline, particularly along the eastern tip of Bradford Island, may be difficult to access by boat for sampler deployment. As a contingency, deployment of samplers from land may be used for these shoreline locations. A handheld GPS will be used to determine land based deployment locations. However, given that deployment of these samplers will be offset by performing a land based deployment, accuracy relative to the target coordinates will be compromised relative to boat based deployment.

Retrieval

Samplers will remain in place for approximately 28 days to allow equilibration. Following the field exposures, samplers will be retrieved by hand from the sampling vessel. Marker buoys will be located through visual observation. Once located, the samplers will be retrieved using the buoy lines. At the surface, the mesh envelopes will be separated from the weights and immediately processed for shipping to TTU. The date, time, and GPS locations will be recorded at the time of retrieval. Missing sampler or

major discrepancies between the deployment and retrieval coordinates will be noted. Discrepancies between deployment and retrieval coordinates may indicate that the samplers were moved by currents during the 28 day deployment period. This uncertainty in location will be noted in the final results and accounted for in the data interpretation.

2.1.4. LPDE Sampler Field Processing

Upon recovery from the field, the PE, while still in the deployment device (e.g., stainless steel mesh), will be carefully cleaned (e.g., remove adhering sediment). The PE will be removed from the mesh and cleaned again with DI water, split into two sections as replicates and each replicate placed in pre-cleaned, amber, glass vials with a few drops of water for shipping. All field processing of LDPE sheets will occur on a clean surface covered in aluminum foil inside the boat cabin. All samplers will be handled while wearing clean nitrile gloves. Subsequent lab processing will be conducted immediately (within 24 hours) of being received in the analytical laboratory.

Table 8. Methods, Sample Containers, Quantities, Volumes, Preservation, and Holding Times

Analytes	Analytical Method	Container type/quantity	Preservation (all 4°C ± 2°C)	Minimum Mass per Sample	Holding Time	Number of field samples	Number of MS/MSD and Field Blanks	Total number of samplers
Subset of PCB Congeners	GC-TQMS (Agilent 7890B) using SIM/SIM mode (EPA Method 1668c)	LDPE sheet (2 x 5*10 cm sheets)	A few drops of water	100 mg	Not extracted:5 days at 4°C Exctracted: 1 year at -20°C	170 (163 –sediment; 5 water column; 2 backup)	5	175

2.1.5. Decontamination Procedures

New powder-free nitrile gloves will be donned at all times when handling LDPE sheets. Upon retrieval of samplers, if any sediment is brought up with the sampling equipment, equipment will be rinsed from the side of the boat before bringing sampling device onto the boat deck.

2.1.6. Field Equipment Calibration, Maintenance, Testing and Inspection Procedures

No field equipment requires calibration, maintenance, testing and inspection. If any sampling procedures are changed to include use of field equipment, that information will be included in the field notes.

2.1.7. Supply Inspection and Acceptance Procedures

Inspection and acceptance of supplies and consumables will be conducted prior to field work in order to ensure that the appropriate type and quantity of supplies are brought to the field. Any supplies and consumables used in the sample collection process or instrument calibration will be inspected.

2.1.8. Field Documentation Procedures

Field documentation provides a permanent record of field activities and can be used, if necessary, to trace possible introduction of field sampling error.

Field notes will be maintained either in a bound logbook, or on field sampling log sheets. After fieldwork is complete, electronic copies will be made of the field notes and the electronic copies will be stored in the project files. All information pertinent to the sampling effort will be recorded in the field notes. Documentation in the field notes will be at a level of detail sufficient to explain and reconstruct field activities without relying on recollection by the field team members. The Field Sampling Lead has overall responsibility for accuracy and completeness of field notes. Each page/form will be consecutively numbered. All entries will be made in indelible ink and corrections will consist of lined-out deletions. As a minimum, the applicable items for the entry into the field notes are listed below.

General Information

- Date
- Start and finish times of work
- Weather conditions
- Name and signature of person making entry
- Names of personnel present

Sampling Information

- Date and time of sample
- Location of sample
- Type of sample
- General river flow direction and velocity
- Water depth

- Sample identification number
- Associated QC samples
- Any unusual observations

2.1.9. Sample Delivery

Sample delivery procedures include packaging, labeling, and shipment to the laboratory. These procedures are designed (1) to preserve sample quality so that analyses will yield results representative of site conditions, (2) to protect and inform sample handlers, including shippers and laboratory personnel, and (3) to provide a paper trail to allow cross referencing of sample collection locations with analytical results.

All samples will be labeled with its own sample identification number and all other applicable information. Samples will be shipped to TTU at:

c/o Alex Smith, Brad Thornhill
Department of Civil, Environmental and Construction Engineering
Texas Tech University
911 Boston
Lubbock Texas 79409
806.742.3523

2.1.10. Sample Custody

A sample is in "custody" if it is in the actual physical possession of authorized personnel or in a secure area that is restricted to authorized personnel. Custody procedures ensure data authenticity and defensibility. Chain of custody (CoC) forms will accompany sample containers during transit to the laboratory and be checked by the laboratory upon receipt.

2.1.11. Disposal of Investigative Derived Wastes

Personal protective equipment (PPE) for the sampling (consisting of Nitrile gloves) and other disposables used during sample preparation will be packaged in plastic garbage bags and disposed in a solid waste bin. All samples and chemical preservatives will be disposed of as per Texas Tech University hazardous material handling requirements.

2.2. Analytical Tasks

Once samples have been collected, they will be analyzed by the laboratories. The Project Chemist will validate the analytical data.

The following sections address all components of project-specific analytical measurements; method and laboratory-specific QC measurements; acceptance criteria; corrective actions; calibration procedures; equipment and supply maintenance; testing; and inspection requirements. Modifications to approved procedures, alternate procedures, or additional procedures are to be pre-approved in writing by the Project Chemist.

2.2.1. Analytical Methods

See Table 9 for analytical methods that will be used for analysis of LDPE samples. All values detected between the LOD and the LOQ will be "J" flagged and reported as detections.

Table 9. Sample Locations, Media, Methods, Analytes of Interest, and Detection and Reporting Limits

Sample Locations and Media	Method	Analytes	LOD[a]	LOQ/RL[a]
River OU, LDPE	GC-TQMS (Agilent 7890B) using SIM/SIM mode (EPA Method 1668c)	Subset of total (46) PCB Congeners AND Total (130) PCB Congeners	≤1 ng / g PE per congener	≤3.5 ng / g PE per congener

[a]Detection limits (LOD) and reporting limits (RL; also known as limit of quantitation (LOQ) are estimated and may change due to specific laboratory conditions, for example, dilutions.

The following isotopically labeled PCBs will serve as PRCs. The PRCs will be pre-loaded to the LDPE samplers to allow for equilibration correction during post processing analysis. See appendix A for laboratory SOPs related to PRC loading and analysis.

13C-PCB 28
13C-PCB 47
13C-PCB 70
13C-PCB 80
13C-PCB 111
13C-PCB 141
13C-PCB 182

2.2.2. Analytical Instrument Calibration Procedures

Calibration procedures and instrumentation shall be consistent with the requirements of the methods.

2.2.3. Analytical Instrument and Equipment Maintenance, Testing, and Inspection Procedures

Maintenance, testing, and inspection procedures shall be consistent with the requirements of the methods.

2.3. Quality Control Samples

Quality control (QC) samples are collected and analyzed for the purpose of assessing the quality of the sampling and analysis performed by the field personnel and the primary laboratory. The Project Chemist will coordinate selection of QC samples prior to each sampling event.

2.3.1. Field Quality Control Samples

2.3.1.1. Field Quality Control Samples

Field samples analyzed for the purpose of assessing the quality of sampling and analysis are to be submitted blind to the analytical laboratory and referred to as field QC samples.

2.3.1.2. Field Duplicates

No field duplicates will be taken for this sampling due to the small number of samples collected and limited budget.

2.3.1.3. Trip Blanks

No trip blanks will be taken for this sampling event as they are not necessary for the selected methods.

2.3.1.4. Field Blanks

Three field blanks will be taken and stored in the field and processed at time of retrieval in the same manner as field samples

2.3.2. Analytical Method Quality Control Samples

Method QC includes the analyses and activities required to ensure that the analytical system is in control prior to and during an analytical run. Method QC requirements for this project include the following: method blanks, surrogate spikes, matrix spikes/matrix spike duplicate pairs, and laboratory control samples.

2.3.2.1. Method Blanks

Method blanks are composed of organic/analyte-free water processed simultaneously with and under the same conditions as samples through all steps of the analytical procedure. Method blanks verify that the measurement system is free of contamination.

2.3.2.2. Laboratory Control Samples (LCS)

Laboratory control sample (LCSs) are composed of organic/analyte-free water spiked with verified amounts of analytes. They are generally used to establish intra-laboratory or analyst-specific precision or to assess the performance of all or a portion of the measurement system. The LCS is analyzed in the same manner as a sample, including preservation.

2.3.2.3. Matrix Spike and Matrix Spike Duplicate (MS/MSD)

MS/MSD samples are used to evaluate matrix interference and to determine laboratory accuracy and precision. Five MS/MSD samples have been identified by TTU for this effort.

2.3.2.4. Surrogates

Surrogates are substances with properties that mimic the analyte of interest. A surrogate is unlikely to be found in environment samples, and is therefore added to them for quality control purposes.

3. ASSESSMENT AND OVERSIGHT

Laboratory and field operations have established policies and procedures, and they designate authorities for implementing corrective action when nonconforming work or departures from the policies and procedures in the quality system or technical operations have been identified. Both field and laboratory operations shall follow all corrective action requirements in methods and SOPs.

The following laboratory documentation is to be made accessible to the USACE Project Chemist. Corrective actions may be required, at the request of USACE, for the following conditions:

- Laboratory Procedures
- QC data outside the defined acceptance windows for precision or accuracy
- Blanks or Laboratory Control Samples (LCS) that contain contaminants above acceptable levels stated in the Data Quality Objectives
- Undesirable trends in spike or surrogate recoveries or RPD between spiked duplicates
- Unusual changes in method detection limits
- Deficiencies identified during internal or external audits or from the results of performance

The following corrective actions should be taken for common problems:

Incoming Samples - Problems noted during sample receipt are to be documented. The USACE Project Chemist is to be notified for problem resolution.

Sample Holding Times - If a maximum holding time is or may be exceeded by the laboratory, the USACE Project Chemist must be notified for problem resolution. The USACE Project Chemist may require re-sampling for the requested parameters.

Instrument Calibration - Sample analysis may not proceed until initial calibrations meet method criteria. Calibrations must meet method time requirements or recalibration must be performed. Continuing calibrations that do not meet accuracy criteria should result in a review of the calibration, rerun of the appropriate calibration standards, and reanalysis of samples affected back to the previous acceptable calibration check.

Limit of Quantitation (LOQ) - Appropriate sample clean-up procedures must be employed to attempt to achieve the practical quantitation limits as stated in the method. If difficulties arise in achieving these limits due to a particular sample matrix, the laboratory should notify the USACE Project Chemist of the problem for resolution. Dilutions are to be documented in the case narrative along with the revised practical quantitation limits for those analytes directly affected. Analytes detected above the method detection limits (MDLs) but below the practical limit(s) of quantitation are to be reported as estimated values and qualified "J".

Method Quality Control - Results related to method QC, including blank contamination, duplicate measurement reproducibility, MS/MSD recoveries, surrogate recoveries, LCS recoveries, and other method-specified QC measures are to meet the laboratory's SOPs and PQOs specified in this plan. Otherwise, the affected samples may be reanalyzed and/or re-extracted and reanalyzed within method-required holding times to verify the presence or absence of matrix effects. In order to confirm matrix

effects, QC results must observe the same direction and magnitude (ten times) bias. The USACE Project Chemist should be notified as soon as possible to discuss appropriate corrective action.

Calculation Errors - Reports must be reissued if calculation and/or reporting errors are noted with any given data package. The case narrative is to state the reason(s) for re-issuance of a report.

4. DATA MANANGEMENT AND DOCUMENTATION

4.1. QAPP

An electronic copy of the QAPP (including appendices) will be stored in USACE project files and provided to the Technical Advisory Group.

4.2. Final Report

Upon completion of the sampling event and receipt/review of the validated data, USACE will prepare a final report. The report may be issued separately, or as an appendix to a future report that addresses source control. The report will include the following:

- Narrative and timeline of project activities
- Summary of sampling, chemical testing, and any deviations from the QAPP
- Analytical data summary and discussion
- Figures, tables, and appendices

The appendices will include field logs, laboratory analytical reports, data validation reports, and data summary tables with associated validation flags.

4.3. Laboratory Documentation (Data Package Deliverables)

4.3.1. Data Package Deliverables

The analytical data packages from the laboratories will be provided to the USACE Seattle Project Chemist as Stage 4 or similar deliverables. The analytical data packages will be validated to Stage 2A or similar by the Project Chemist for 100% of all samples analyzed by the laboratory.

4.3.2. Electronic Data Reporting Formats

The laboratory data will be provided in Microsoft Excel format. A copy of the laboratory data will be provided to the Technical Advisory Group upon completion of the data validation.

5. DATA REVIEW, VERIFICATION, AND VALIDATION

Data review is the process by which data are examined and evaluated to varying levels of detail and specificity by a variety of personnel who have different responsibilities within the data management process. It includes verification, validation, and usability assessment. This process ensures the review

activities produce scientifically sound data that are of known and documented quality and meet PQOs used in making environmental decisions.

5.1. Review of Laboratory Data

All laboratory data packages will include raw data necessary for full validation. Analytical data packages will be validated to Stage 2A or similar by the USACE Seattle Project Chemist for 100% of all samples analyzed by the contracted laboratory (TTU).

Three distinct evaluative steps will be used to ensure that project-specific data quality needs are met:

- Data Verification (review for completeness) – Confirmation by examination and provision of objective evidence that the specified requirements (sampling and analytical) have been completed.

- Data Validation – Confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use are fulfilled. Validation is a sampling and analytical process that includes evaluating compliance with method, procedure, or contract requirements and extends to evaluating against criteria based on the quality objectives developed in the QAPP (e.g., the QAPP measurement performance criteria). The purpose of validation is to assess the performance of the sampling and analysis processes to determine the quality of specified data. Data Validation Reports will be generated for each sampling event.

- Data Usability Assessment – Determination of the adequacy of data, based on the results of validation and verification, and professional judgment by the Project Chemist, for the decisions being made. The usability step involves assessing whether the process execution and resulting data meet project quality objectives documented in the QAPP.

Data review will be based on laboratory-specific SOPs conforming to the method and applying the principles of the EPA National Functional Guidelines for Organic and Inorganic Data Review (EPA 2008). If significant deviations arise as a result of initial verification and validation, the level of review will be elevated in order to determine the source and impact of deviations.

5.2. Data Verification and Validation Stages

Data validation and verification stages described below are in accordance with US EPA Guidance for Labeling Externally Validated Laboratory Analytical Data for Superfund Use (EPA QA-R-08-005; 2009).

5.2.1. Stage 1

Verification and validation begins with Stage 1 checks of the laboratory analytical data package consisting of compliance of sample receipt conditions, sample characteristics (e.g., percent moisture), and analytical results (with associated information). The following minimum baseline checks (as relevant) shall be performed on the laboratory analytical data package received for a Stage 1 validation label:

(1) Documentation identifies the laboratory receiving and conducting analyses, and includes documentation for all samples submitted by the project or requested for analyses.

(2) Requested analytical methods were performed and the analysis dates are present.

(3) Requested target analyte results are reported along with the original laboratory data qualifiers and data qualifier definitions for each reported result (and the uncertainty of each result and clear indication of the type of uncertainty reported if required).

(4) Requested target analyte result units are reported.

(5) Requested reporting limits for all samples are present and results at and below the project-specific reporting limits are clearly identified (including sample detection limits if required).

(6) Sampling dates (including times if needed), date and time of laboratory receipt of samples, and sample conditions upon receipt at the laboratory (including preservation, pH and temperature) are documented.

(7) Sample results are evaluated by comparing sample conditions upon receipt at the laboratory (e.g., preservation checks) and sample characteristics (e.g., percent moisture) to the requirements and guidelines present in national or regional data validation documents, analytical method(s) or contract.

5.2.2. Stage 2A

Stage 2A validation builds on the validation conducted in Stage 1. Stage 2A validation of the laboratory analytical data package consists of the Stage 1 validation plus the verification and validation checks for the compliance of sample-related QC. The following additional minimum baseline checks (as relevant) shall be performed on the laboratory analytical data package received for a Stage 2A Validation label:

(8) Requested methods (handling, preparation, cleanup, and analytical) are performed.

(9) Method dates (including dates, times and duration of analysis for radiation counting measurements and other methods, if needed) for handling (e.g., Toxicity Characteristic Leaching Procedure), preparation, cleanup and analysis are present, as appropriate.

(10) Sample-related QC data and QC acceptance criteria (e.g., method blanks, surrogate recoveries, deuterated monitoring compounds (DMC) recoveries, laboratory control sample (LCS) recoveries, duplicate analyses, matrix spike and matrix spike duplicate recoveries) are provided and linked to the reported field samples (including the field quality control samples such as trip and equipment blanks).

(11) Requested spike analytes or compounds (e.g., surrogate, DMCs, LCS spikes) have been added, as appropriate.

(12) Sample holding times (from sampling date to preparation and preparation to analysis) are evaluated.

(13) Frequency of QC samples is checked for appropriateness (e.g., one LCS per twenty samples in a preparation batch).

(14) Sample results are evaluated by comparing holding times and sample-related QC data to the requirements and guidelines present in national or regional data validation documents, analytical method(s) or contract.

5.2.3. Stage 2B

Stage 2B validation builds on the validation conducted in Stage 2A. Stage 2B validation of the laboratory analytical data package consists of the Stage 2A validation plus the verification and validation checks for the compliance of instrument-related QC. The following additional minimum baseline checks (as relevant) shall be performed on the laboratory analytical data package received for a Stage 2B Validation label:

(15) Initial calibration data (e.g., initial calibration standards, initial calibration verification [ICV] standards, initial calibration blanks [ICBs]) are provided for all requested analytes and linked to field samples reported. For each initial calibration, the calibration type used is present along with the initial calibration equation used including any weighting factor(s) applied and the associated correlation coefficients, as appropriate. Recalculations of the standard concentrations using the initial calibration curve are present, along with their associated percent recoveries, as appropriate (e.g., if required by the project, method, or contract). For the ICV standard, the associated percent recovery (or percent difference, as appropriate) is present.

(16) Appropriate number and concentration of initial calibration standards are present.

(17) Continuing calibration data (e.g., continuing calibration verification [CCV] standards and continuing calibration blanks [CCBs]) are provided for all requested analytes and linked to field samples reported, as appropriate. For the CCV standard(s), the associated percent recoveries (or percent differences, as appropriate) are present.

(18) Reported samples are bracketed by CCV standards and CCBs standards as appropriate.

(19) Method specific instrument performance checks are present as appropriate (e.g., tunes for mass spectrometry methods).

(20) Frequency of instrument QC samples is checked for appropriateness (e.g., gas chromatography-mass spectroscopy [GC-MS] tunes have been run every 12 hours).

(21) Sample results are evaluated by comparing instrument-related QC data to the requirements and guidelines present in national or regional data validation documents, analytical method(s) or contract.

5.2.4. Stage 3

Stage 3 validation builds on the validation conducted in Stage 2B. Stage 3 validation of the laboratory analytical data package consists of the Stage 2B validation plus the recalculation of instrument and sample results from the laboratory instrument responses, and comparison of recalculated results to laboratory reported results. The following additional minimum baseline checks (as relevant) shall be performed on the laboratory analytical data package received for a Stage 3 Validation label:

(22) Instrument response data (e.g., GC peak areas) are reported for requested analytes, surrogates, internal standards, and DMCs for all requested field samples, matrix spikes, matrix spike duplicates, LCS, and method blanks as well as calibration data and instrument QC checks (e.g., tunes).

(23) Reported target analyte instrument responses are associated with appropriate internal standard analyte(s) for each (or selected) analyte(s) (for methods using internal standard for calibration).

(24) Fit and appropriateness of the initial calibration curve used or required (e.g., mean calibration factor, regression analysis [linear or non-linear, with or without weighting factors, with or without forcing]) is checked with recalculation of the initial calibration curve for each (or selected) analyte(s) from the instrument response.

(25) Comparison of instrument response to the minimum response requirements for each (or selected) analyte(s).

(26) Recalculation of each (or selected) opening and closing CCV (and CCB) response from the peak data reported for each (or selected) analyte(s) from the instrument response, as appropriate.

(27) Compliance check of recalculated opening and/or closing CCV (and CCB) response to recalculated initial calibration response for each (or selected) analyte(s).

(28) Recalculation of percent ratios for each (or selected) tune from the instrument response, as appropriate.

(29) Compliance check of recalculated percent ratio for each (or selected) tune from the instrument response.

(30) Recalculation of each (or selected) instrument performance check (e.g., instrument blanks,) from the instrument response.

(31) Recalculation and compliance check of retention time windows (for chromatographic methods) for each (or selected) analyte(s) from the laboratory reported retention times.

(32) Recalculation of reported results for each reported (or selected) target analyte(s) from the instrument response.

(33) Recalculation of each (or selected) reported spike recovery (surrogate recoveries, DMC recoveries, LCS recoveries, duplicate analyses, matrix spike and matrix spike duplicate recoveries) from the instrument response.

(34) Each (or selected) sample result(s) and spike recovery(ies) are evaluated by comparing the recalculated numbers to the laboratory reported numbers according to the requirements and guidelines present in national or regional data validation documents, analytical method(s) or contract.

Note: Selection of analytes, spikes, and performance evaluation checks for the Stage 3 validation checks for a laboratory analytical data package being verified and validated generally will depend on many factors including (but not limited to) the type of verification and validation being performed (manual or

electronic), requirements and guidelines present in national or regional data validation documents, analytical method(s) or contract, the number of laboratories reporting the data, the number and type of analytical methods reported, the number of analytes reported in each method, and the number of detected analytes.

5.2.5. Stage 4

Stage 4 validation builds on the validation conducted in Stage 3. Stage 4 validation of the laboratory analytical data package consists of the Stage 3 validation plus the evaluation of instrument outputs. The following additional minimum baseline checks (as relevant) shall be performed on the laboratory analytical data package received for a Stage 4 Validation label:

(35) All required instrument outputs (e.g., chromatograms, mass spectra) for evaluating sample and instrument performance are present.

(36) Sample results are evaluated by checking each (or selected) instrument output (e.g., chromatograms, mass spectra) for correct identification and quantitation of analytes (e.g., peak integrations, use of appropriate internal standards for quantitation, elution order of analytes, and interferences).

(37) Each (or selected) instrument's output(s) is evaluated for confirmation of non-detected or tentatively identified analytes.

Selection of instrument outputs for the Stage 4 validation checks for a laboratory analytical data package being verified and validated generally will depend on many factors including, but not limited to, the type of verification and validation being performed (electronic or manual), requirements and guidelines present in national or regional data validation documents, analytical method(s) or contract, the number of laboratories reporting the data, the number and type of analytical methods reported, the number of analytes reported in each method, and the number of detected analytes.

5.3. Data Verification and Validation Stages

A data validation report will be generated by the USACE Chemist that encompasses the results of the manual review of private lab data. The data validation report will be an appendix to the Final Report. Professional judgment shall be used when deciding if qualification of data is applicable. When professional judgment is applied, the rationale shall be provided. Tables of qualified data and the reasons for qualification will also be included in the data validation report.

Qualifiers will be added to data during the review as necessary. Qualifiers applied to the data as a result of the review are as follows:

U Indicates the compound or analyte was analyzed for but not detected at or above the stated limit. The data are usable for decision-making purposes.

UJ Indicates the compound or analyte was analyzed for but not detected. Due to a quality control deficiency identified during data validation, the value reported may not accurately reflect the

sample quantitation limit. The associated value is considered estimated, but the data are generally usable for decision-making purposes.

J Indicates the compound or analyte was analyzed for and detected. The associated value is estimated due to a quality control deficiency identified during data validation. False positives or false negatives are unlikely to have been reported and the data are generally usable for decision-making purposes.

J+ Data are qualified as estimated with a high bias. False positives are likely to occur but the data are generally usable for decision-making purposes.

J- Data are qualified as estimated with a low bias. False negatives are likely to occur but the data are generally usable for decision-making purposes.

R The sample results are rejected due to serious deficiencies in the ability to analyze the sample and meet quality control criteria. The presence or absence of the analyte cannot be verified.

Note: It is possible that J-qualified data are not suitable for some purposes. For example, a J-qualified concentration with a low bias that is just below a screening value may not be usable to determine whether the analyte concentration is above or below the screening value. The effect of the use of qualified data on the decision-making process must be evaluated as part of the "reconciliation with user requirements" process.

5.4. Usability Assessment

The Project Chemist will evaluate overall precision, accuracy, completeness, representativeness, comparability, and sensitivity of the sampling data; including an assessment of the overall usability of the data and describing any limitations on its use. The Project Chemist will summarize any audit information, indicating corrective actions taken. This information will be part of the data validation report, which is an appendix to the Final Report.

6. REFERENCES

U.S. Army Corps of Engineers. 2019. *Final Work Plan for Passive Sampling at River OU, Bradford Island, Cascade Locks, Oregon.* September 30, 2019.

U.S. Environmental Protection Agency. 2009. *Intergovernmental Data Quality Task Force Uniform Federal Policy for Quality Assurance Project Plans Guidance.*

U.S. Environmental Protection Agency. 2008. *Contract Laboratory Program National Functional Guidelines for Superfund Organic Methods Data Review.*

URS. 2012. *Upland and River Operable Units Remedial Investigation Report, Bradford Island, Cascade Locks, Oregon.*

Appendix A

Standard Operating Procedure for the Extraction and Analysis of Polyethylene (PE) Used in Polyethylene Devices (PEDs)

Originally Developed by Philip M. Gschwend and John K. MacFarlane, MIT

As adapted for use in the laboratories of Danny Reible, Texas Tech University

Standard Operating Procedure for the Extraction and Analysis of Polyethylene (PE) Used in Polyethylene Devices (PEDs)

1.0 SCOPE AND APPLICATION

1.1 This method describes procedures for chemical analysis of contaminants contained in polyethylene (PE) that has been deployed in passive samplers used to assess hydrophobic organic compounds (HOCs) in environmental media.

1.2 This procedure generates extracts suitable for High Resolution Gas Chromatography/Mass Spectrometry (GCMS) analysis.

1.3 This extraction procedure is applicable to PE used in laboratory (ex situ) - or field (in situ)-exposed usage.

1.4 Procedures for loading PE with PRCs are discussed in a companion SOP, "Standard Operating Procedure for the Preparation of Polyethylene (PE) Used for Passive Sampling"

2.0 SUMMARY OF METHOD

2.1 Upon recovery from the field, the PE, while still in the deployment device (e.g., stainless steel mesh or aluminum frame), should be carefully cleaned (e.g., remove adhering sediment) and then cut into appropriate lengths (e.g., to obtain replicates or to acquire sections exposed to varying depths into a sediment bed). The PE pieces, usually 10 to 100 milligram quantities, are placed in pre-cleaned, amber, glass vials with a few drops of water for shipping. Once received by the analytical laboratory, each sample is spiked with Surrogate standards (to assess analyte recoveries) and submerged in a suitable solvent (e.g., methylene chloride) for at least 12 hours. The extract is quantitatively transferred to a large vessel suited for solvent evaporation, and then the PE is re-extracted two more times with methylene chloride, with the extracts combined for evaporative concentration and eventual GCMS (or suitable) instrumental analysis. After extraction, the PE is air-dried and weighed.

2.2 A shaker table or other suitable system is recommended for the extractions to facilitate PE-solvent contact.

3.0 INTERFERENCES

3.1 PE is susceptible to contamination from atmospheric and surficial sources, and so it must be handled using clean techniques.

3.2 While the sediment solids, biofilms, and inorganic precipitates on PE surfaces does not prevent HOC accumulation in the PE during in situ deployment, these coatings can substantially complicate subsequent chemical analysis. Careful removal of adhering sediment or surface growths via wiping with a water-wetted Kimwipe® may be necessary. Surface coatings of organic films on PE (e.g., oil or tar residues) can be removed without compromising the sample by using solvent-saturated wipes (<minute

contact times) followed by immediate Surrogate standard addition and solvent extraction.

4.0 APPARATUS AND MATERIALS

4.1 Extraction vessels: amber glass vials (foil-lined lids)

4.2 Concentrating vessels: 100 mL glass, pear-shaped flask with glass stopper; 250 mL glass, round-bottom flask with glass stopper or equivalent

4.3 Bottle/jar tumbler, shaker table, bottle roller or equivalent

4.4 Analytical balance - capable of weighing to 0.1 mg (i.e., small value relative to samplers weights that are typically between 10 and 100 mg).

4.5 Food-grade aluminum foil

4.6 Stainless steel forceps

4.7 Single-edge razor blades

4.8 Teflon (or similar non-contaminating material) cutting board

4.9 Glass transfer pipettes

4.10 Kimberly-Clark Kimwipe® or equivalent

5.0 REAGENTS

5.1 Methylene chloride, CH_2Cl_2, pesticide grade or equivalent (other solvent suited to analytes of interest).

5.2 Organic-free reagent water (as defined in SW-846 Chapter One)

5.3 Research grade surrogate and injection standard compounds certified >98+% pure or equivalent.

6.0 PREPARATION AND HANDLING

6.1 Upon recovery and return to a clean working environment, the PE should be surface cleaned prior to any cutting or extraction. The PE surface should be wiped and rinsed free of surface particles and coatings as much as possible. This may include briefly (< minute) wiping with a hexane-soaked Kimwipe® (or equivalent) to remove oily or tarry exterior staining. If water wet, the PE surface should be blotted dry with a clean wipe.

6.2 Laboratory and field personnel should wear nitrile or latex gloves whenever handling PE to avoid cross-contaminating the PE.

6.3 Methylene chloride (pesticide grade) rinsed, stainless steel forceps and scissors are used when manipulation of PE is required.

6.4 Clean aluminum foil is used to cover any surface that PE may encounter.

7.0 PROCEDURE

7.1 Solvent Extraction: Laboratory and/or field blank and field-exposed PE is spiked with known quantities of surrogate compounds to assess analytical recoveries and extracted using organic solvents prior to analysis by GC/MS.

7.1.1 The PE is inspected for surface biofilms, particles, mud, or oily coatings. Biofilm mass should be removed as much as possible by using a clean wipe followed by a rinse with organic-free reagent water. Particles and sedimentary debris are removed by rinsing with organic-free reagent water and careful surface scraping if necessary to remove adhered/imbedded material. Oily coatings (e.g., coal tar staining or hydrocarbon slicks) are removed by soaking clean wipes in hexane and using forceps to hold and wipe both PE surfaces. This is not an exhaustive extraction and should be done quickly (<minute) and immediately prior to immersion in solvent. PE surfaces are blotted dry if water wet.

7.1.2 The PE is transferred to a pre-cleaned amber vial (size determined by dimensions of PE, typically 15-40 mL). Vial must be large enough for complete immersion of PE without excessive PE folding.

7.1.3 Known masses of surrogate compounds (Appendix 1) in a methylene chloride-compatible solvent are added to the vial. Typical additions are: 2.5-20 ng for aqueous samples; 50-250 ng for sediment samples, depending on target HOCs and their expected concentrations in the PE.

7.1.4 Methylene chloride is added to the vial to completely submerge the PE for a period of at least 12 hours.

7.1.5 The extract is transferred to a pre-cleaned glass concentration vessel. A second aliquot of methylene chloride is added to the extraction vial and agitated for >10 minutes. This step is repeated two more times.

7.1.6 After the final extract transfer, the PE is dried in air dry in the extraction vial and then weighed on an analytical balance until a consistent PE mass is obtained. This result is used to calculate the final target HOC concentrations measured in the PE sampler in units of HOC mass per PE mass.

7.2 Extracts are concentrated using rotary evaporation (or equivalent) down to suitable volumes for GCMS analysis; the resultant concentrated extracts are transferred to smaller vials (e.g., for autosamplers) according to standard laboratory practices. Before analysis, appropriate injection standards are added to the final extracts to allow for evaluation of the total volume of extract analyzed (Appendix 1).

Typical final extract volumes are:

50-250 μL for water column-exposed PE

1-4 mL for contaminated sediment bed-exposed PE

8.0 QUALITY CONTROL

8.1 Method blanks, field blanks, matrix spikes, and/or replicate samples should be subjected to exactly the same analytical procedures as those used on field/lab-exposed PE samples.

8.2 QA/QC metrics, that are specific to the type of target HOCs of interest and the analytical methods used to quantify them, should be applied. Typical values for targets, like PAHs and PCBs, that are analyzed by capillary gas chromatography-low resolution mass spectrometry, in which picogram/uL detection is common, are:

8.2.1 Freshly prepared polyethylene and trip blanks: <0.1 ng HOC / g PE
Freshly cleaned PE samples, and samples of PE that traveled to and from the field site ("trip blank"), should have no significant peaks where PRCs, surrogate standards, injection standards, and target analytes elute.

8.2.2 PRC-loaded polyethylene reproducibility (±1σ/mean, N=6): <10%
Individual batches of PE loaded with PRCs should exhibit reproducible PRC concentrations in the PE before deployment.

:

8.2.3 Recoveries of Surrogate Standards: >70% to < 120%
Surrogate standards should be recovered from PE samples at nearly 100%, plus or minus analytical precision. An exception may be relatively volatile compounds (e.g., mono-, di-chlorobiphenyls, naphthalene) that may be significantly lost when extracts are evaporated (e.g., recovery down to 60%).

8.2.4 Precision of replicate PE extract analyses (N≥3): <25%.
The reproducibility of all analytes (injection standards, surrogate standards, PRCs, and target compounds) determined with multiple instrumental analyses of the same PE sample extract, even run on different dates, should fall within suitably narrow bounds.

8.2.5 Detection limits using PE samples: ≤1 ng / g PE
Assuming 100 mg PE samples and 100 uL final extract volumes, target analytes, such as PAHs and PCBs, analyzed by GCMS (or methods with like sensitivity) should have <ppb detection limits.

9.0 METHOD PERFORMANCE

9.1 The method performance is assessed by determining the recovery and reproducibility in analyzing surrogate compounds (Appendix 1). All other lab-specific QA/QC metrics should be adhered to.

9.2 Successful PE deployment is achieved when significant (>method precision) losses of PRCs occurred, allowing one to use their behavior to adjust target compound levels in the PE up to equilibrium concentrations (Fernandez et al. 2009; Tcaciuc et al. 2014).

10.0 REFERENCES

Fernandez L.A., Harvey, C.F., and Gschwend, P.M. Using performance reference compounds in polyethylene passive samplers to deduce sediment pore water concentrations for numerous target chemicals. Environ. Sci. Technol., 43, 8888-8894, 2009.

Tcaciuc, AP, JN Apell, and PM Gschwend. " Passive Sampler PRC Calculation Software and User's Guide". Available at https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200915. July 2014.

Appendix 1 Suggested Performance Reference Compounds (PRCs), Surrogate Compounds (Recovery Standards), and Injection Standards. The laboratory preparing the PE must coordinate PRC choices with the laboratory doing the PE analyses to avoid conflicting uses.

A. PRCs, suitable for polycyclic aromatic hydrocarbon (PAH) determinations when Capillary Gas Chromatography-Mass Spectrometry (GCMS) is used for analysis include, but are not restricted to, deuterated PAHs. One subset should be used as PRCs, while reserving others for use as surrogate (recovery) and injection standards. Unlabeled compounds such as terphenyl can be used as injection standards if they are readily resolved from the other analytes.

Targets: PAHs	**Method: GCMS**	**Detection Limit ~ 100 pg / 100 mg PE**	
PRCs	^{13}C6-phenanthrene, ^{13}C6-fluoranthene, ^{13}C6-chrysene, ^{13}C6-indeno(1,2,3-cd)pyrene		
Surrogates	d10-anthracene	d10-fluoranthene	d12-benz(a)anthracene
Injection Standards	d10-acenaphthene	d14-*m*-terphenyl	d12-perylene

B. PRCs and surrogate compounds suitable for polychlorinated biphenyl (PCB) determinations when GCMS is the method separation and detection include, but are not restricted to, ^{13}C-labeled or deuterated PCB congeners. One subset, for example including tri-, tetra-, penta-, hexa-, and heptachloro-biphenyls, can be used as PRCs while reserving different tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl congeners to serve as surrogate compounds. Still other compounds such as deuterated PAHs or rare PCBs (not contained in Aroclor/Clophan mixtures such as: PCB-39, PCB-55, PCB-104, PCB-150 and PCB-188) can be used as injection standards.

Targets: PCBs	**Method: GCMS**	**Detection Limit ~ 100 pg / 100 mg PE**
PRCs	^{13}C labelled PCB congeners: 37, 47, 54, 111, 138, 178	
Surrogates	^{13}C labelled PCB congeners: 3, 15, 28, 52, 118, 153, 180, 194, 208, 209	
Injection Standards	^{13}C labelled PCB congeners: 19, 105, 170	

C. When analyzing for organochlorine pesticides such as DDT using GCMS, ^{13}C labeled compounds can serve as PRCs. However, since DDT has been seen to degrade to form DDE or DDD in certain situations, one should use the 4,4'- isomer of DDT and the 2,4'-isomers of DDE and DDD as PRCs to allow appearance of 13C-labelled 4,4'-DDE of 4,4'-DDD to be interpreted as arising from reaction the DDT PRC during the deployment. Deuterated or ^{13}C labeled PCBs can be used as surrogate (recovery) and injection standards.

Targets: DDTs	**Method: GCMS**	**Detection Limit ~ 200 pg / 100 mg PE**	
PRCs	^{13}C 2,4'-DDE	^{13}C 2,4'-DDD	^{13}C 4,4'-DDT
Surrogates	^{13}C-PCB111	^{13}C-PCB153	^{13}C PCB 178
Injection Standards	d6 PCB 77	^{13}C PCB 105	^{13}C PCB 167

Standard Operating Procedure for the Extraction and Analysis of Polyethylene (PE) Used in Polyethylene Devices (PEDs)

Originally Developed by Philip M. Gschwend and John K. MacFarlane, MIT

As adapted for use in the laboratories of Danny Reible, Texas Tech University

Standard Operating Procedure for the Extraction and Analysis of Polyethylene (PE) Used in Polyethylene Devices (PEDs)

1.0 SCOPE AND APPLICATION

1.1 This method describes procedures for chemical analysis of contaminants contained in polyethylene (PE) that has been deployed in passive samplers used to assess hydrophobic organic compounds (HOCs) in environmental media.

1.2 This procedure generates extracts suitable for High Resolution Gas Chromatography/Mass Spectrometry (GCMS) analysis.

1.3 This extraction procedure is applicable to PE used in laboratory (ex situ) - or field (in situ)-exposed usage.

1.4 Procedures for loading PE with PRCs are discussed in a companion SOP, "Standard Operating Procedure for the Preparation of Polyethylene (PE) Used for Passive Sampling"

2.0 SUMMARY OF METHOD

2.1 Upon recovery from the field, the PE, while still in the deployment device (e.g., stainless steel mesh or aluminum frame), should be carefully cleaned (e.g., remove adhering sediment) and then cut into appropriate lengths (e.g., to obtain replicates or to acquire sections exposed to varying depths into a sediment bed). The PE pieces, usually 10 to 100 milligram quantities, are placed in pre-cleaned, amber, glass vials with a few drops of water for shipping. Once received by the analytical laboratory, each sample is spiked with Surrogate standards (to assess analyte recoveries) and submerged in a suitable solvent (e.g., methylene chloride) for at least 12 hours. The extract is quantitatively transferred to a large vessel suited for solvent evaporation, and then the PE is re-extracted two more times with methylene chloride, with the extracts combined for evaporative concentration and eventual GCMS (or suitable) instrumental analysis. After extraction, the PE is air-dried and weighed.

2.2 A shaker table or other suitable system is recommended for the extractions to facilitate PE-solvent contact.

3.0 INTERFERENCES

3.1 PE is susceptible to contamination from atmospheric and surficial sources, and so it must be handled using clean techniques.

3.2 While the sediment solids, biofilms, and inorganic precipitates on PE surfaces does not prevent HOC accumulation in the PE during in situ deployment, these coatings can substantially complicate subsequent chemical analysis. Careful removal of adhering sediment or surface growths via wiping with a water-wetted Kimwipe® may be necessary. Surface coatings of organic films on PE (e.g., oil or tar residues) can be removed without compromising the sample by using solvent-saturated wipes (<minute

contact times) followed by immediate Surrogate standard addition and solvent extraction.

4.0 APPARATUS AND MATERIALS

4.1 Extraction vessels: amber glass vials (foil-lined lids)

4.2 Concentrating vessels: 100 mL glass, pear-shaped flask with glass stopper; 250 mL glass, round-bottom flask with glass stopper or equivalent

4.3 Bottle/jar tumbler, shaker table, bottle roller or equivalent

4.4 Analytical balance - capable of weighing to 0.1 mg (i.e., small value relative to samplers weights that are typically between 10 and 100 mg).

4.5 Food-grade aluminum foil

4.6 Stainless steel forceps

4.7 Single-edge razor blades

4.8 Teflon (or similar non-contaminating material) cutting board

4.9 Glass transfer pipettes

4.10 Kimberly-Clark Kimwipe® or equivalent

5.0 REAGENTS

5.1 Methylene chloride, CH_2Cl_2, pesticide grade or equivalent (other solvent suited to analytes of interest).

5.2 Organic-free reagent water (as defined in SW-846 Chapter One)

5.3 Research grade surrogate and injection standard compounds certified >98+% pure or equivalent.

6.0 PREPARATION AND HANDLING

6.1 Upon recovery and return to a clean working environment, the PE should be surface cleaned prior to any cutting or extraction. The PE surface should be wiped and rinsed free of surface particles and coatings as much as possible. This may include briefly (< minute) wiping with a hexane-soaked Kimwipe® (or equivalent) to remove oily or tarry exterior staining. If water wet, the PE surface should be blotted dry with a clean wipe.

6.2 Laboratory and field personnel should wear nitrile or latex gloves whenever handling PE to avoid cross-contaminating the PE.

6.3 Methylene chloride (pesticide grade) rinsed, stainless steel forceps and scissors are used when manipulation of PE is required.

6.4 Clean aluminum foil is used to cover any surface that PE may encounter.

7.0 PROCEDURE

7.1 Solvent Extraction: Laboratory and/or field blank and field-exposed PE is spiked with known quantities of surrogate compounds to assess analytical recoveries and extracted using organic solvents prior to analysis by GC/MS.

7.1.1 The PE is inspected for surface biofilms, particles, mud, or oily coatings. Biofilm mass should be removed as much as possible by using a clean wipe followed by a rinse with organic-free reagent water. Particles and sedimentary debris are removed by rinsing with organic-free reagent water and careful surface scraping if necessary to remove adhered/imbedded material. Oily coatings (e.g., coal tar staining or hydrocarbon slicks) are removed by soaking clean wipes in hexane and using forceps to hold and wipe both PE surfaces. This is not an exhaustive extraction and should be done quickly (<minute) and immediately prior to immersion in solvent. PE surfaces are blotted dry if water wet.

7.1.2 The PE is transferred to a pre-cleaned amber vial (size determined by dimensions of PE, typically 15-40 mL). Vial must be large enough for complete immersion of PE without excessive PE folding.

7.1.3 Known masses of surrogate compounds (Appendix 1) in a methylene chloride-compatible solvent are added to the vial. Typical additions are: 2.5-20 ng for aqueous samples; 50-250 ng for sediment samples, depending on target HOCs and their expected concentrations in the PE.

7.1.4 Methylene chloride is added to the vial to completely submerge the PE for a period of at least 12 hours.

7.1.5 The extract is transferred to a pre-cleaned glass concentration vessel. A second aliquot of methylene chloride is added to the extraction vial and agitated for >10 minutes. This step is repeated two more times.

7.1.6 After the final extract transfer, the PE is dried in air dry in the extraction vial and then weighed on an analytical balance until a consistent PE mass is obtained. This result is used to calculate the final target HOC concentrations measured in the PE sampler in units of HOC mass per PE mass.

7.2 Extracts are concentrated using rotary evaporation (or equivalent) down to suitable volumes for GCMS analysis; the resultant concentrated extracts are transferred to smaller vials (e.g., for autosamplers) according to standard laboratory practices. Before analysis, appropriate injection standards are added to the final extracts to allow for evaluation of the total volume of extract analyzed (Appendix 1).

Typical final extract volumes are:

50-250 μL for water column-exposed PE

1-4 mL for contaminated sediment bed-exposed PE

8.0 QUALITY CONTROL

8.1 Method blanks, field blanks, matrix spikes, and/or replicate samples should be subjected to exactly the same analytical procedures as those used on field/lab-exposed PE samples.

8.2 QA/QC metrics, that are specific to the type of target HOCs of interest and the analytical methods used to quantify them, should be applied. Typical values for targets, like PAHs and PCBs, that are analyzed by capillary gas chromatography-low resolution mass spectrometry, in which picogram/uL detection is common, are:

8.2.1 Freshly prepared polyethylene and trip blanks: <0.1 ng HOC / g PE
Freshly cleaned PE samples, and samples of PE that traveled to and from the field site ("trip blank"), should have no significant peaks where PRCs, surrogate standards, injection standards, and target analytes elute.

8.2.2 PRC-loaded polyethylene reproducibility (±1σ/mean, N=6): <10%
Individual batches of PE loaded with PRCs should exhibit reproducible PRC concentrations in the PE before deployment.

:

8.2.3 Recoveries of Surrogate Standards: >70% to < 120%
Surrogate standards should be recovered from PE samples at nearly 100%, plus or minus analytical precision. An exception may be relatively volatile compounds (e.g., mono-, di-chlorobiphenyls, naphthalene) that may be significantly lost when extracts are evaporated (e.g., recovery down to 60%).

8.2.4 Precision of replicate PE extract analyses (N≥3): <25%.
The reproducibility of all analytes (injection standards, surrogate standards, PRCs, and target compounds) determined with multiple instrumental analyses of the same PE sample extract, even run on different dates, should fall within suitably narrow bounds.

8.2.5 Detection limits using PE samples: ≤1 ng / g PE
Assuming 100 mg PE samples and 100 uL final extract volumes, target analytes, such as PAHs and PCBs, analyzed by GCMS (or methods with like sensitivity) should have <ppb detection limits.

9.0 METHOD PERFORMANCE

9.1 The method performance is assessed by determining the recovery and reproducibility in analyzing surrogate compounds (Appendix 1). All other lab-specific QA/QC metrics should be adhered to.

9.2 Successful PE deployment is achieved when significant (>method precision) losses of PRCs occurred, allowing one to use their behavior to adjust target compound levels in the PE up to equilibrium concentrations (Fernandez et al. 2009; Tcaciuc et al. 2014).

10.0 REFERENCES

Fernandez L.A., Harvey, C.F., and Gschwend, P.M. Using performance reference compounds in polyethylene passive samplers to deduce sediment pore water concentrations for numerous target chemicals. Environ. Sci. Technol., 43, 8888-8894, 2009.

Tcaciuc, AP, JN Apell, and PM Gschwend. " Passive Sampler PRC Calculation Software and User's Guide". Available at https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-200915. July 2014.

Appendix 1 Suggested Performance Reference Compounds (PRCs), Surrogate Compounds (Recovery Standards), and Injection Standards. The laboratory preparing the PE must coordinate PRC choices with the laboratory doing the PE analyses to avoid conflicting uses.

A. PRCs, suitable for polycyclic aromatic hydrocarbon (PAH) determinations when Capillary Gas Chromatography-Mass Spectrometry (GCMS) is used for analysis include, but are not restricted to, deuterated PAHs. One subset should be used as PRCs, while reserving others for use as surrogate (recovery) and injection standards. Unlabeled compounds such as terphenyl can be used as injection standards if they are readily resolved from the other analytes.

Targets: PAHs	**Method: GCMS**	**Detection Limit ~ 100 pg / 100 mg PE**	
PRCs	^{13}C6-phenanthrene, ^{13}C6-fluoranthene, ^{13}C6-chrysene, ^{13}C6-indeno(1,2,3-cd)pyrene		
Surrogates	d10-anthracene	d10-fluoranthene	d12-benz(a)anthracene
Injection Standards	d10-acenaphthene	d14-*m*-terphenyl	d12-perylene

B. PRCs and surrogate compounds suitable for polychlorinated biphenyl (PCB) determinations when GCMS is the method separation and detection include, but are not restricted to, ^{13}C-labeled or deuterated PCB congeners. One subset, for example including tri-, tetra-, penta-, hexa-, and heptachloro-biphenyls, can be used as PRCs while reserving different tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl congeners to serve as surrogate compounds. Still other compounds such as deuterated PAHs or rare PCBs (not contained in Aroclor/Clophan mixtures such as: PCB-39, PCB-55, PCB-104, PCB-150 and PCB-188) can be used as injection standards.

Targets: PCBs	**Method: GCMS**	**Detection Limit ~ 100 pg / 100 mg PE**
PRCs	^{13}C labelled PCB congeners: 37, 47, 54, 111, 138, 178	
Surrogates	^{13}C labelled PCB congeners: 3, 15, 28, 52, 118, 153, 180, 194, 208, 209	
Injection Standards	^{13}C labelled PCB congeners: 19, 105, 170	

C. When analyzing for organochlorine pesticides such as DDT using GCMS, ^{13}C labeled compounds can serve as PRCs. However, since DDT has been seen to degrade to form DDE or DDD in certain situations, one should use the 4,4'- isomer of DDT and the 2,4'-isomers of DDE and DDD as PRCs to allow appearance of 13C-labelled 4,4'-DDE of 4,4'-DDD to be interpreted as arising from reaction the DDT PRC during the deployment. Deuterated or ^{13}C labeled PCBs can be used as surrogate (recovery) and injection standards.

Targets: DDTs	**Method: GCMS**	**Detection Limit ~ 200 pg / 100 mg PE**	
PRCs	^{13}C 2,4'-DDE	^{13}C 2,4'-DDD	^{13}C 4,4'-DDT
Surrogates	^{13}C-PCB111	^{13}C-PCB153	^{13}C PCB 178
Injection Standards	d6 PCB 77	^{13}C PCB 105	^{13}C PCB 167

Standard Operating Procedure for the Preparation of Polyethylene (PE) Used for Passive Sampling

Originally Developed by Philip M. Gschwend and John K. MacFarlane, MIT

As adapted for use in the laboratories of Danny Reible, Texas Tech University

Standard Operating Procedure for the Preparation of Polyethylene (PE) Used for Passive and Active Sampling of HOCs

1.0 SCOPE AND APPLICATION

1.1 This method describes a procedure for preparing and handling polyethylene (PE) films that will be cut into strips and deployed to sample hydrophobic organic compounds (HOCs) in environmental media.

1.2 This method generates PE that can be deployed for passive or active (i.e., using mixing) sampling of HOCs in atmospheric, aqueous, or sediment-porewater systems.

1.3 PE that is prepared by this method is suitable for *ex situ* laboratory or *in situ* field deployment.

2.0 SUMMARY OF METHOD

2.1 A known mass of low density polyethylene (LDPE) sheet, usually gram quantities, is cleaned by sequentially extracting with methylene chloride, methanol, and ultrapure water in a closed glass vessel.

2.2 Clean PE is equilibrated with performance reference compounds (PRCs) dissolved in water or methanol-water (see Appendix 1 for possible PRCs).

2.3 PRC-impregnated PE is stored in water or aqueous PRC loading solution in glass vessels until use.

2.4 Shortly before deployment, the PE is cut into suitably sized strips and prepared for deployment.

2.5 During deployment, the PE is exposed to the environmental medium of concern. HOCs in the medium diffuse into the PE, while PRCs diffuse out.

3.0 INTERFERENCES

3.1 PE is susceptible to contamination from atmospheric vapors and contact with surfaces (e.g., worker hands), so it must remain in clean sealed vessels until deployment.

4.0 APPARATUS AND MATERIALS

4.1 Extraction vessels: 1-L glass bottles or screw capped jars (foil-lined lids).

4.2 Storage vessels: bottles with glass stoppers or amber jars (foil-lined lids).

4.3 Bottle/jar tumbler, shaker table, bottle roller, or equivalent.

4.4 Low density polyethylene (LDPE): commercial grade, large sheet at 25μm (1 mil) or 51μm (2 mil) thickness. The thickness is chosen to be strong enough to withstand stresses during deployment (e.g., insertion into sediment), but thin enough to exchange a significant fraction (e.g., >20%) of its PRCs during the deployment time to be used.

4.5 Food grade aluminum foil (solvent cleaned and/or combusted to remove any organic residue from foil production)

4.6 Stainless steel forceps

4.7 Teflon (or similar non-contaminating material) cutting board

5.0 REAGENTS

5.1 Methylene chloride, CH_2Cl_2, pesticide grade or equivalent

5.2 Methanol, CH_3OH, pesticide grade or equivalent

5.3 Organic-free reagent water (as defined in SW-846 Chapter 1)

5.4 Research grade PRCs certified >98+% pure.

Note: Specific standard materials, concentrations, solvents, and solvent purity requirements must be determined based upon the target HOCs of concern and their likely concentrations in any particular application.

6.0 PRESERVATION AND HANDLING

6.1 Clean PE should be stored in clean, sealed, glass vessels.

6.2 PE loaded with PRCs should be stored in sealed glass containers that contain either:

(a) a few mL of organic-free reagent water added to maintain 100% relative humidity within the storage vessels (minimizing sorptive losses of PRCs to glass vessel walls),

(b) completely filled with organic-free reagent water (common after loading from aqueous methanol solutions), or

(c) still filled with the aqueous PRC-loading solution (preferred, but may lead to shipping concerns).

6.3 Laboratory and field personnel should wear nitrile or latex gloves whenever handling clean PE.

6.4 Methylene chloride-rinsed, stainless steel forceps and scissors are used when manipulation of clean PE is required.

6.5 Methylene chloride-rinsed, aluminum foil is used to cover any surface that clean PE may encounter.

7.0 PROCEDURE

7.1 Polyethylene Cleaning Procedure: LDPE is purchased from hardware/painting stores in large sheets ('dropcloth or plastic tarp' material) with thickness of 25μm (1 mil) or 51μm (2 mil), depending on the user's need for strength (choose thicker) and desire to use short deployment times (use thinner). The sheet is cut into strips sized for the environment and deployment apparatus to be used. An organic solvent cleaning sequence is then used to prepare the PE. This process ensures that extractable oligomers, plasticizers, and contaminating organic chemicals are removed from the PE prior to use. All extractions are performed sequentially in the same container.

7.1.1 Methylene chloride is placed into the extraction vessel, and the PE strips are immersed in the container for 24 hours to enable time for diffusive transfers out of the PE. The initial methylene chloride extract is discarded and a second

methylene chloride extraction is performed for 24 hours. The second methylene chloride extract is discarded and replaced by methanol to remove methylene chloride from the PE. Methanol immersion is also done for 24 hours. The initial methanol extract is discarded and followed by a second methanol soak for 24 hours. Finally, the second methanol extract is discarded and the PE undergoes three 24-hour soaks with organic-free reagent water (within the same extraction vessel) to remove residual methanol from the PE.

7.1.2 The cleaned PE is stored in organic-free reagent water in the extraction vessel until further processing.

7.2 Polyethylene Preparation with Performance Recovery Compounds (PRCs): PRCs are loaded into the clean PE, prior to its field deployment, by utilizing either aqueous (Fernandez et al. 2009) or 20:80 or 80:20 methanol:water equilibrations (Booij et al., 2002). Note that 20:80 methanol:water ratios can speed equilibration relative to the aqueous approach but partitioning of the PRCs should be assumed similar to aqueous solutions. Depending on the hydrophobic organic compounds of interest, PRCs should be chosen to mimic mass transfer phenomena governing exchanges during field deployments. It is important to avoid adding PRCs that the analytical laboratory already uses as surrogate recovery, cleanup, or injection standards. PRC loading is performed by placing the PE in pre-cleaned glass vessels containing known PRC solutions made up in organic-free reagent water with or without pesticide-grade methanol. (The methanol swells the PE, enabling faster PRC uptake; but use of methanol also requires post PRC-impregnation removal of the methanol from the PE by soaking in water.) The PE user should load the PE with levels of PRCs that are a little greater than the concentrations of target HOCs that are expected to be accumulated from the environment, thereby facilitating the eventual chemical analyses. The PRC concentrations loaded in the PE can be found using each PRC's PE-water partition coefficient (e.g., Burgess et al. 2017) and the ratio of the PE mass to the aqueous solution volume of the loading solution. For example, one may set out to load 1 g of PE using an aqueous solution containing 10 ug of a PRC in a liter of water, so the ratio of PE to water, r_{PEw} , is 1/1000 . If that PRC's K_{PEw} is 10^5 $(ug/g_{PE})/(ug/mL_w)$, then one finds the fraction of that PRC that ends up in the 1 g of PE as:

$$f_{PE} = (r_{PEw})(K_{PEw})/(1+ r_{PEw}K_{PEw})$$

$$= (1\ g_{PE}/1000\ mL_w)(10^5 mL_w/g_{PE})/[1 + (1\ g_{PE}/1000\ mL_w)(10^5 mL_w/g_{PE})]$$

$$= 0.99$$

or 9.9 ug of the PRC is in the PE at equilibrium (i.e., 9.9 ug_{PRC}/g_{PE})

and the water concentration has dropped to 0.1 ug_{PRC}/L_w .

7.3 Sufficient PRC equilibration time during this PE preparation step is necessary to ensure uniform PE loading across the entire PE thickness; hence thicker PE sheet is more robust for field use, but takes longer to load with PRCs. If previously untested PRCs are used, a time course study should be used to performed to confirm PE-

solution equilibration of the PRCs (e.g., Booij et al. 2002).

7.3.1 Isotopically labeled compounds are useful PRCs, surrogate recovery standards, and injection standards when Gas Chromatography-Mass Spectrometry (GCMS) is the method of separation and detection. For example, deuterated polycyclic aromatic hydrocarbons (PAHs) and C13-labeled PCBs are effective methodological standards for PE passive sampling. If PAHs are the target contaminants, one subset of compounds, distributed across the range of PAHs to be assessed (e.g., d10-phenanthrene, d10-pyrene, and d12-chrysene), should be used as PRCs, while another set (e.g., d10-anthracene, d10-fluoranthene, and d12-benz(a)anthracene) is used as surrogate (recovery) compounds during later analysis of laboratory or field-deployed PE. Finally, still another set of compounds (e.g., d10-acenaphthene, d14-*m*-terphenyl, and d12-perylene) should be used as injection standards. Similar sets of labeled compounds should be used for other compound classes (see Appendix 1). Note: if PE samples are eventually to be analyzed at a contract laboratory, PRC choices must be made so as not to conflict with recovery and injection standards used by that laboratory.

7.3.2 As subsequent analysis (e.g., GCMS) is best achieved with both PRCs and target HOCs present at like concentrations in the PE extracts, the optimal concentration level of the PRC loaded into the PE is dependent on the environment in which the PE is to be deployed. For example, if a target HOC is expected to occur in the water or pore water near 1 ng/L levels, one can use that compound's LDPE-water partition coefficient (e.g., Fernandez et al., 2009; Lohmann, 2012; Burgess et al. 2017) to estimate the expected levels in the PE after deployment:

$$\text{Concentration in PE (ng/kg)} \sim K_{PE\text{-}water} * \text{concentration in (pore)water (ng/L)}$$

For example, if the $K_{PE\text{-}water}$ for the target HOC of interest is 10^5 (L/kg), then the concentration of the target HOC in the PE will approach 100 ug/kg as it equilibrates with water at 1 ng/L. Based on this estimate, the PRCs are loaded into the PE at slightly higher (e.g., factor of 2) concentrations since some fraction of these will be lost from the PE during deployment. Appendix 2 shows a typical calculation used to design a PRC-containing MeOH:H_2O solution of PCBs suited to loading an 0.82 g mass of PE (i.e., one or more PE pieces summing to 0.82 g) to achieve about 100 ug of each PRC per kg of PE.

7.3.3 Aqueous PRC Loading: A solvent-cleaned and dried glass container is filled with ultrapure water that has been spiked with known concentrations of PRCs (e.g., based on calculations like those shown in Appendix 2). A known mass of pre-cleaned PE is then added and weighted to insure complete PE submersion. The vessel is agitated to remove any air pockets/bubbles adhering to the submerged PE. Equilibration times vary for different PRC/PE thickness combinations and the PE-water phase ratio. For PAHs and PCBs, one should use at least 30 days to insure homogeneous distributions of the PRCs throughout the entire thickness of the PE film unless faster equilibration has been confirmed with PRC/PE specific time-course testing of PRC concentrations in the PE or by showing that concentrations of PRCs are the same for films of different thicknesses, but the same masses. Generally, PE is stored in the PRC solution until that PE is to be deployed.

7.3.4 Methanol-Aided PRC Loading: A solvent-cleaned and dried glass container is filled with a mixture of pesticide grade methanol and ultrapure water (e.g., Booij et al. 2002) that has been spiked with known concentrations of PRCs (e.g., see calculations in Appendix 2). A known mass of pre-cleaned PE is then added and weighted to insure complete submersion. The vessel should be agitated to remove any bubbles/air pockets adhering to the submerged PE. Equilibration times vary for different PRC/PE thickness combinations and the PE-solvent phase ratio, but typically this step is completed within 7 days since methanol swells the PE and thereby speeds PRC diffusion into the polymer sheet (Booij et al., 2002). Generally, the PE is stored in the PRC solution until shortly before it is to be deployed. Before deployment, the PRC-loaded PE is rinsed with ultrapure water, and then it is soaked in ultrapure water for 24 h to remove most of the methanol from the PE, while leaving the more hydrophobic PRCs almost completely in the PE. This methanol leaching step is repeated twice to insure complete methanol removal.

8.0 QUALITY CONTROL

8.1 PRC Loading Validation: At least six representative samples of prepared PE should be collected from different parts of the PRC-loaded PE (e.g., 1 cm x 10 cm x 25 um pieces weighing about 25 mg each), extracted, and analyzed prior to field deployment to validate that the PRC concentrations are consistent with their intended loadings and these PRCs have uniform concentrations in a batch of PE.

8.2 Target HOC Blanks: Subsamples of prepared PE, commensurate in size with the planned environmental PE samples (e.g., 10 cm wide by 5 cm long by 25 um thick and therefore weighing about 120 mg), should be be collected, extracted, and analyzed prior to field deployment to demonstrate that other substances have not contaminated the PE which would contribute to interfering background for the target HOCs analysis using the intended target analyte detection approach.

9.0 METHOD PERFORMANCE

9.1 PRC data, obtained from PE samples collected from >six pieces of the prepared PE, should be consistent within about ±10% (i.e., 100 x standard deviation / mean).

9.2 Target HOC concentrations should be undetectable in the prepared PE at the levels of interest. For example, , assuming a target HOC with a level of interest at 10 pg/L = 10^{-5} ng/mL$_{water}$ and having $K_{PE\ water}$ = 10^{5} mL$_{water}$/g PE , requires background below:

(level of interest) x $K_{LDPE\ water}$ = 1 ng HOC /g PE.

10.0 REFERENCES

Adams, R.G., Lohmann, R., Fernandez L.A., MacFarlane, J.K., and Gschwend, P.M., Environ. Sci. & Technol. 2007, 41, 1317-1323.

Booij, K, Smedes, F., van Weerlee, E.M., Chemosphere 2002, 46, 1157-1161.

Burgess, R.M., Kane Driscoll, S.B., Burton, G.A., Ghosh, U., Gschwend, P.M., Reible, D., Ahn, S., and Thompson, T. Laboratory, Field, and Analytical Procedures for Using Passive Sampling in the Evaluation of Contaminated Sediments: User's Manual. EPA/600/R-16/357. 153 pp. 2017.

Fernandez, LA, MacFarlane, J.K., Tcaciuc, A.P., and Gschwend, P.M., Environ. Sci. & Technol; 2009, 43, 1430-1436.

Hawker DW and Connell DW. 1988. Environ. Sci. Technol. 22: 382-387.

Lohmann, R. MacFarlane, J.K. and Gschwend, P.M., Environ. Sci. & Technol; 2005, 39, 141-148.

Lohmann, R. Environ. Sci. & Technol.; 2012, 46, 606–618.

Appendix 1 Suggested Performance Reference Compounds (PRCs), Surrogate Compounds (Recovery Standards), and Injection Standards.

A. PRCs, suitable for polycyclic aromatic hydrocarbon (PAH) determinations when Gas Chromatography-Mass Spectrometry (GCMS) is the preferred method of detection, include, but are not restricted to, deuterated PAH compounds. One subset should be used as PRCs, while reserving others for use as surrogate (recovery) compounds. Still other compounds such as terphenyl can be used as injection standards.

Targets: PAHs	**Method: EPA 8270d with GCMS-SIM**			
PRCs	d10-phenanthrene	d10-pyrene	d12-chrysene	d12-benzo(b)fluoranthene
Surrogates	d10-anthracene	d10-fluoranthene	d12-benz(a)anthracene	d12-perylene
Injection Standards	d10-acenaphthene	d14-*m*-terphenyl		

B. PRCs and surrogate compounds suitable for polychlorinated biphenyl (PCB) determinations when GCMS is the preferred method of detection include, but are not restricted to, ^{13}C-labeled or deuterated PCB congeners. One subset, for example including a tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl, can be used as PRCs while reserving different tri-, tetra-, penta-, hexa-, and heptachloro-biphenyl congeners to serve as surrogate compounds (see below) and injection standards.

Targets: PCBs	**Method: EPA 8270d with GCMS-SIM**					
PRCs	^{13}C PCB-37	^{13}C PCB-47	^{13}C PCB-54	^{13}C PCB-111	^{13}C PCB-138	^{13}C PCB-178
log K_{ow}	5.68	5.87	5.32	6.49	6.71	6.98
number Cl's	3	4	4	5	6	7
Surrogates number Cl's	^{13}C PCB-3 1	^{13}C PCB-15 2	^{13}C PCB-28 3	^{13}C PCB-52 4	^{13}C PCB-118 5	^{13}C PCB-153 6
Surrogates number Cl's		^{13}C PCB-180 7	^{13}C PCB-194 8	^{13}C PCB-208 9	^{13}C PCB-209 10	

Injection Standards	^{13}C PCB-19	^{13}C PCB-105	^{13}C PCB-170			

C. When analyzing for organochlorine pesticides such as DDT using GCMS, ^{13}C labeled compounds can serve as PRCs and surrogate standards. Since DDT has been shown to degrade to form DDE or DDD in certain situations, one should use the 4,4'-isomer of DDT and the 2,4'-isomers of DDE and DDD as PRCs to allow appearance of ^{13}C-labelled 4,4'-DDE of 4,4'-DDD to be interpreted as arising from reaction of the DDT PRC during the deployment. Deuterated or ^{13}C labeled PCBs can be used as surrogate (recovery) and injection standards.

Targets: DDTs	**Method: GCMS**	**Detection Limit ~ 200 pg / 100 mg PE**	
PRCs	^{13}C 2,4'-DDE	^{13}C 2,4'-DDD	^{13}C 4,4'-DDT
Surrogates	^{13}C-PCB111	^{13}C-PCB153	^{13}C 2,4'-DDT
Injection Standards	d6 PCB 77	^{13}C PCB 105	^{13}C PCB 167

Appendix 2. Example of spreadsheet used to design a PRC solution needed to impregnate PE for PCB sampling.

Step 1: Find/estimate PE-spiking solvent partition coefficients for PRCs in solvents of interest (see spreadsheet below). Here 80:20 MeOH:H_2O values from Booij et al. (2002) are used to develop a correlation with K_{ow} values from the literature (Hawker and Connell, 1988); this relation is then used to estimate $K_{PE\text{-}(80:20)m:w}$ values for other PCB congeners partitioning between PE and an 80:20 MeOH:water solution.

Step 2: Choose the size of PE needed for the sampling exercise (here a single 1 mil-thick strip of 5 cm width and 68 cm length) and solve for the PE mass (here 0.82 g). Choose a vessel which is large enough to fit the PE inside without extensive PE-PE surface contact, but small enough so that unacceptably expensive masses of the labeled PRCs are not used (here 125 mL ground glass stopped flask). For this PE mass and solution volume, use the PE-solution partition coefficients from step 1 to solve for the fractions of each PRC that will be in the PE at equilibrium using:

$$\text{fraction in PE} = 1 - (1 / (1+\text{Mass}_{PE}*K_{PE\text{-solution}}/\text{Volume}_{solution})) \qquad \text{Eq. 1}$$

(e.g., 5.8% for congener #52)

Step 3. Solve for spiking solution concentrations of PRCs that result in desired PRC loadings in the PE (here 100 ng/g_{PE}) using:

$$C_{\text{initial spiking solution}} = C_{\text{desired in PE}} * \text{Mass}_{pe} / \text{fraction in PE} / \text{Volume}_{solution} \qquad \text{Eq. 2}$$

(e.g., here we find we need about 11.3 ng congener #52 per mL to achieve 100 ng/g PE; this is concentration of the spiking solution that the investigator must make up to prepare PE for subsequent sampling at sites where it is expected that the (pore)water will cause the PE to accumulate about 10 to 100 ng of target PCBs/g_{PE}). Note that the values vary from PRC to PRC, so one might choose to load from a mean solution concentration (*ca.* 5 ng/mL) if the PRCs are supplied at the same concentrations in a stock solution.

PE is stored in the PRC loading solution until shortly before passive sampling use.

Step 4. If spiking solutions contain organic co-solvents like MeOH, this MeOH must be leached out of the PE before the polymer film can be used for passive sampling. To insure that MeOH leaching will not substantially change PRC loading, one may calculate whether substantial fractions of the PRCs will be lost in subsequent steps required to leach the MeOH from the PE. Since the leaching steps involve use of H_2O (with only a little MeOH from the PE), use the PE-water partition coefficients. For PCBs, these coefficients are derived from a linear free energy relationship (LFER) found in the review by Lohmann (2012). With these values, we can solve for the fractional losses of individual PRCs to each batch of the leachate contained in 1000 mL ground glass stoppered flasks, using:

fraction of each PRC remaining in PE after a single leach step = 1 – (1 / (1+$K_{PE\text{-}H2O}$*Mass $_{PE}$ / Volume $_{H2O}$)) Eq. 3

For example, in the case of congener #52, one finds 99.66% of the PRC remains in the PE after the first leach (see below). Two additional leaches lower this to 99.32% and 98.98%, respectively. More hydrophobic congeners are leached even less in this case.

Example spreadsheet calculation for spiking PCB PRCs into LDPE from a 80:20 methanol-water solution.

step 1						step 2		step 3		step 4			
								Solution concentration			fraction of PRC left in PE after		
						for PE mass (g)	0.82	(ng/mL) in in order to get			each water soak to remove MeOH		
	Training data for estimation of $K_{PE\text{-}(80:20)m:w}$		potential 13C-labelled PCBs to use as PRCs		use correlation to estimate partition coeff'	Volume of MeOH:water (mL)	125	100	ng/g PE	estim log $K_{PE\text{-}w}$	1st leach (Eq. 3)	2nd leach (Eq. 3)	3rd leach (Eq. 3)
PCB congener	log KPE-MeOH:water (ref 1)	log Kow (ref 2)	congener	log Kow (ref 2)	log $K_{PE\text{-}(80:20)m:w}$	fraction of each PRC in PE at equilib' (Eq. 1)		ng/mL MeOH:H2O (Eq. 2)		log Kpew = 1.14*log Kow-1.14 (ref 3)	1000 mL water	1000	1000 mL water
4	0.20	4.65	**52**	5.84	0.97	5.8%		11.3		5.52	0.997	0.993	0.990
29	1.05	5.6	**101**	6.38	1.26	10.7%		6.1		6.13	*minimal leaching back into water*		
155	1.29	6.41	**153**	6.92	1.55	18.8%		3.5		6.75	1.000		
204	1.67	7.3	**180**	7.36	1.78	28.4%		2.3		7.25	1.000		
			28	5.67	0.88	4.8%		13.8		5.32	0.995	0.990	0.985
			47	5.85	0.98	5.9%		11.2		5.53	*minimal leaching back into water*		
			111	6.76	1.46	16.0%		4.1		6.57	1.000		
			153	6.92	1.55	18.8%		3.5		6.75	1.000		
			178	7.14	1.66	23.3%		2.8		7.00	1.000		
use to find following correlation:													
$\log K_{PE\text{-}(80:20)m:w} = 0.532\ (\pm 0.094) * \log K_{ow}$(Hawker) - 2.133 (± 0.57						**PE mass**		5.3	geom ave				
N = 4, R2 = 0.94, S.E. 0.18						number of strips	1						
						PE density (g/cm3)	0.95						
1. Booij, K, Smedes, F., van Weerlee, E.M., Chemosphere 2002, 46, 1157-1161.						PE thickenss (cm)	0.00254	for 1 mil sheet					
2. Hawker DW and Connell DW. 1988. Environ. Sci. Technol. 22: 382-387.						PE length (cm)	68						
3. Lohmann, R. Environ. Sci. & Technol.; 2012, 46, 606–618.						PE width (cm)	5						
						length*width*thickness *number of strips*density							
						mass of PE (g)	**0.82**						

Appendix B

Sample Number	Latitude	Longitude	Sample Type
1	45.642744	-121.939608	Target Sample Location
2	45.642822	-121.939549	Target Sample Location
3	45.64292	-121.939477	Target Sample Location
4	45.642918	-121.939368	Target Sample Location
5	45.642826	-121.939399	Target Sample Location; water column sampler A
6	45.642742	-121.93947	Target Sample Location
7	45.642658	-121.939402	Target Sample Location
8	45.642741	-121.939332	Target Sample Location
9	45.642824	-121.939261	Target Sample Location
10	45.642918	-121.939207	Target Sample Location
11	45.642923	-121.939056	Target Sample Location
12	45.642823	-121.939123	Target Sample Location
13	45.64274	-121.939194	Target Sample Location
14	45.64266	-121.939224	Target Sample Location
15	45.642739	-121.939056	Target Sample Location
16	45.642822	-121.938985	Target Sample Location
17	45.642933	-121.938866	Target Sample Location
18	45.642943	-121.938685	Target Sample Location
19	45.64282	-121.938847	Target Sample Location
20	45.642737	-121.938918	Target Sample Location
21	45.642642	-121.939031	Target Sample Location
22	45.642644	-121.938829	Target Sample Location
23	45.642736	-121.93878	Target Sample Location
24	45.642819	-121.938709	Target Sample Location
25	45.642902	-121.938508	Target Sample Location
26	45.642818	-121.938571	Target Sample Location
27	45.642735	-121.938642	Target Sample Location
28	45.642625	-121.938631	Target Sample Location
29	45.642733	-121.938504	Target Sample Location
30	45.642817	-121.938433	Target Sample Location
31	45.642894	-121.93836	Target Sample Location
32	45.642899	-121.938224	Target Sample Location
33	45.642815	-121.938295	Target Sample Location
34	45.642732	-121.938365	Target Sample Location
35	45.642634	-121.938422	Target Sample Location
36	45.642731	-121.938227	Target Sample Location
37	45.642814	-121.938157	Target Sample Location

38	45.642897	-121.938086	Target Sample Location
Sample Number	**Latitude**	**Longitude**	**Sample Type**
39	45.642896	-121.937948	Target Sample Location
40	45.642813	-121.938019	Target Sample Location; water column sampler B
41	45.64273	-121.938089	Target Sample Location
42	45.642616	-121.93819	Target Sample Location
43	45.64262	-121.937989	Target Sample Location
44	45.642728	-121.937951	Target Sample Location
45	45.642812	-121.937881	Target Sample Location
46	45.642915	-121.937793	Target Sample Location
47	45.642922	-121.937645	Target Sample Location
48	45.642823	-121.937736	Target Sample Location
49	45.642727	-121.937818	Target Sample Location
50	45.642637	-121.937794	Target Sample Location
51	45.642659	-121.937625	Target Sample Location
52	45.642726	-121.937658	Target Sample Location
53	45.642822	-121.937577	Target Sample Location
54	45.642918	-121.937495	Target Sample Location
55	45.642916	-121.937336	Target Sample Location
56	45.64282	-121.937417	Target Sample Location
57	45.642724	-121.937499	Target Sample Location
58	45.642656	-121.937446	Target Sample Location
59	45.642723	-121.937339	Target Sample Location
60	45.642819	-121.937258	Target Sample Location
61	45.642911	-121.937181	Target Sample Location
62	45.642902	-121.937019	Target Sample Location
63	45.642817	-121.937098	Target Sample Location
64	45.642731	-121.937204	Target Sample Location
65	45.642636	-121.937283	Target Sample Location
66	45.642677	-121.937123	Target Sample Location
67	45.64273	-121.936976	Target Sample Location
68	45.642816	-121.936938	Target Sample Location
69	45.6429	-121.936866	Target Sample Location
70	45.642905	-121.936712	Target Sample Location
71	45.642814	-121.936779	Target Sample Location
72	45.642732	-121.936788	Target Sample Location
73	45.642734	-121.936607	Target Sample Location
74	45.642813	-121.936619	Target Sample Location

75	45.642908	-121.936552	Target Sample Location
76	45.642907	-121.936396	Target Sample Location
Sample Number	**Latitude**	**Longitude**	**Sample Type**
77	45.642811	-121.93646	Target Sample Location
78	45.642753	-121.936436	Target Sample Location
79	45.64281	-121.9363	Target Sample Location
80	45.642908	-121.936245	Target Sample Location; water column sampler C
81	45.642894	-121.93615	Target Sample Location
82	45.642791	-121.936189	Target Sample Location
83	45.642815	-121.936086	Target Sample Location
84	45.642903	-121.936	Target Sample Location
85	45.642968	-121.935946	Target Sample Location
86	45.642996	-121.935805	Target Sample Location
87	45.642912	-121.935888	Target Sample Location
88	45.642846	-121.935933	Target Sample Location
89	45.642845	-121.935821	Target Sample Location
90	45.64292	-121.935769	Target Sample Location
91	45.642994	-121.935678	Target Sample Location
92	45.642923	-121.935673	Target Sample Location
93	45.642844	-121.935708	Target Sample Location
94	45.642777	-121.935766	Target Sample Location
95	45.642775	-121.935653	Target Sample Location
96	45.642843	-121.935596	Target Sample Location
97	45.642916	-121.935558	Target Sample Location
98	45.642995	-121.935502	Target Sample Location
99	45.642993	-121.935402	Target Sample Location
100	45.642909	-121.935448	Target Sample Location
101	45.642842	-121.935483	Target Sample Location
102	45.642774	-121.935541	Target Sample Location
103	45.642841	-121.93537	Target Sample Location
104	45.642908	-121.935316	Target Sample Location
105	45.642984	-121.935293	Target Sample Location
106	45.642986	-121.935192	Target Sample Location
107	45.642906	-121.935214	Target Sample Location
108	45.64284	-121.935258	Target Sample Location
109	45.642771	-121.935203	Target Sample Location
110	45.642839	-121.935145	Target Sample Location; water column sampler D
111	45.642907	-121.935115	Target Sample Location

112	45.642992	-121.935071	Target Sample Location
113	45.642998	-121.934943	Target Sample Location
114	45.642913	-121.935	Target Sample Location
Sample Number	**Latitude**	**Longitude**	**Sample Type**
115	45.642838	-121.935033	Target Sample Location
116	45.64277	-121.93509	Target Sample Location
117	45.642698	-121.935068	Target Sample Location
118	45.64261	-121.935044	Target Sample Location
119	45.642569	-121.934979	Target Sample Location
120	45.642837	-121.93492	Target Sample Location
121	45.642914	-121.93488	Target Sample Location
122	45.642998	-121.934828	Target Sample Location
123	45.642922	-121.934771	Target Sample Location
124	45.64292	-121.934654	Target Sample Location
125	45.64285	-121.934728	Target Sample Location
126	45.642774	-121.934768	Target Sample Location
127	45.642657	-121.934791	Target Sample Location
128	45.642578	-121.934818	Target Sample Location
129	45.642516	-121.934886	Target Sample Location
130	45.642481	-121.934774	Target Sample Location
131	45.64256	-121.934712	Target Sample Location
132	45.642629	-121.934643	Target Sample Location
133	45.642743	-121.934643	Target Sample Location
134	45.642834	-121.934582	Target Sample Location
135	45.642926	-121.934531	Target Sample Location
136	45.642926	-121.934394	Target Sample Location
137	45.642835	-121.934459	Target Sample Location
138	45.642721	-121.934518	Target Sample Location
139	45.642628	-121.934498	Target Sample Location
140	45.642552	-121.934573	Target Sample Location
141	45.642479	-121.934651	Target Sample Location
142	45.642401	-121.934747	Target Sample Location
143	45.642299	-121.934844	Target Sample Location
144	45.642225	-121.934808	Target Sample Location
145	45.642295	-121.934752	Target Sample Location
146	45.642376	-121.934627	Target Sample Location
147	45.642467	-121.934547	Target Sample Location
148	45.642516	-121.934452	Target Sample Location

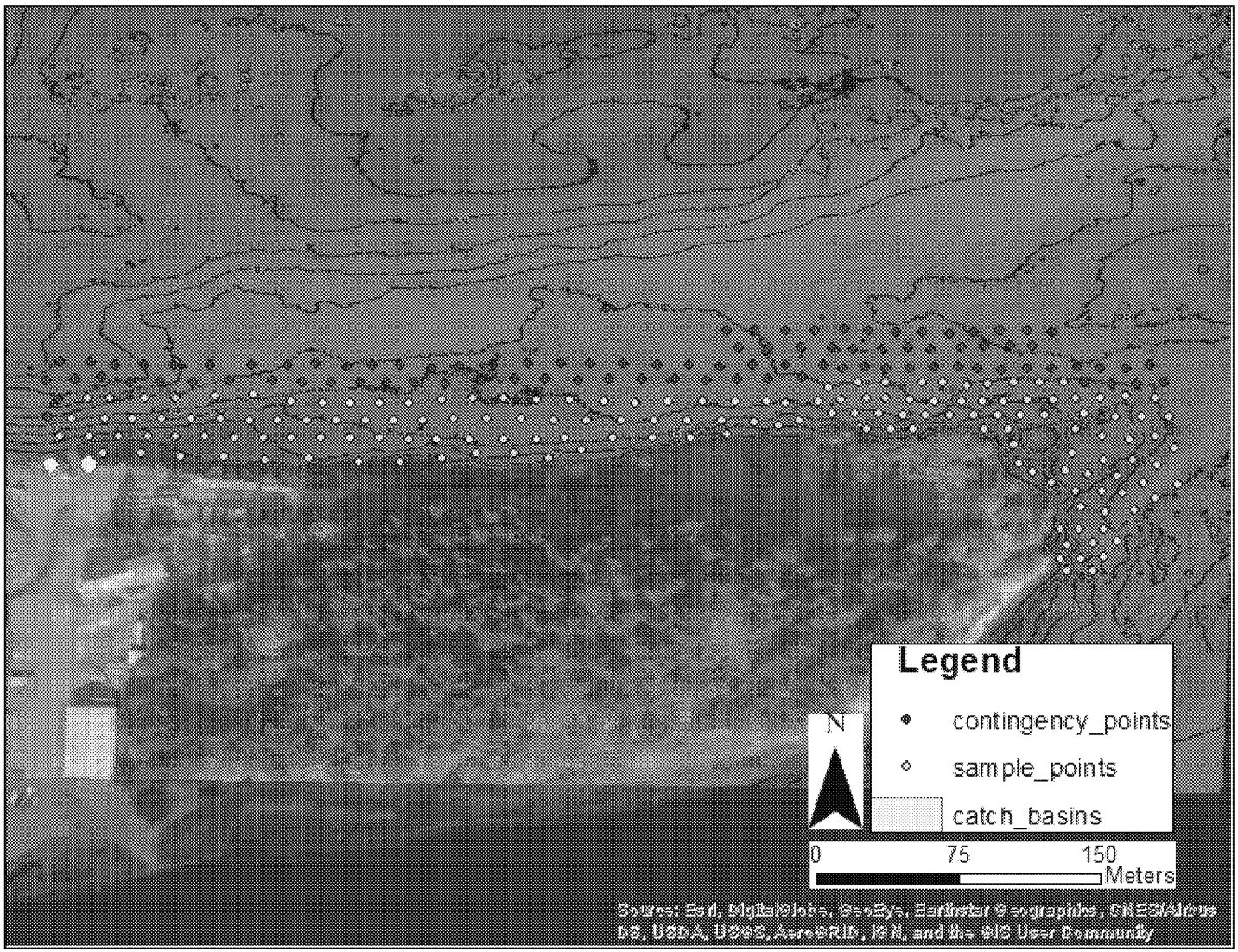
149	45.642604	-121.93438	Target Sample Location
150	45.642739	-121.934396	Target Sample Location
151	45.642828	-121.934329	Target Sample Location
152	45.642685	-121.934302	Target Sample Location
Sample Number	**Latitude**	**Longitude**	**Sample Type**
153	45.64251	-121.934288	Target Sample Location
154	45.642446	-121.934392	Target Sample Location
155	45.642384	-121.934489	Target Sample Location
156	45.642297	-121.934641	Target Sample Location
157	45.642227	-121.934692	Target Sample Location
158	45.642943	-121.938685	Target Sample Location
159	45.642161	-121.934641	Target Sample Location
160	45.642156	-121.934748	Target Sample Location; water column sampler E
161	45.64216	-121.934844	Target Sample Location
162	45.642098	-121.934811	Target Sample Location
163	45.642097	-121.934691	Target Sample Location
164	45.642832	-121.939666	Primary Contingecy Location
165	45.642917	-121.939619	Primary Contingecy Location
166	45.643005	-121.939677	Primary Contingecy Location
167	45.643091	-121.939608	Primary Contingecy Location
168	45.64301	-121.939534	Primary Contingecy Location
169	45.643093	-121.93946	Primary Contingecy Location
170	45.643019	-121.939415	Primary Contingecy Location
171	45.643082	-121.939344	Primary Contingecy Location
172	45.643	-121.939275	Primary Contingecy Location
173	45.643079	-121.939207	Primary Contingecy Location
174	45.642993	-121.939137	Primary Contingecy Location
175	45.64308	-121.939063	Primary Contingecy Location
176	45.642998	-121.938975	Primary Contingecy Location
177	45.643079	-121.938898	Primary Contingecy Location
178	45.643002	-121.938805	Primary Contingecy Location
179	45.643078	-121.938696	Primary Contingecy Location
180	45.643003	-121.938599	Primary Contingecy Location
181	45.643081	-121.938525	Secondary Contingency Location
182	45.642999	-121.938461	Secondary Contingency Location
183	45.643083	-121.938389	Secondary Contingency Location
184	45.642994	-121.938319	Secondary Contingency Location
185	45.643074	-121.938242	Secondary Contingency Location
186	45.642992	-121.938178	Secondary Contingency Location
187	45.643079	-121.938118	Secondary Contingency Location
188	45.642995	-121.938054	Secondary Contingency Location
189	45.643074	-121.937987	Secondary Contingency Location
190	45.642994	-121.93792	Secondary Contingency Location
191	45.643061	-121.937843	Secondary Contingency Location
192	45.642991	-121.937773	Secondary Contingency Location

193	45.643072	-121.937706	Secondary Contingency Location
194	45.643008	-121.937604	Secondary Contingency Location
195	45.643082	-121.937545	Secondary Contingency Location
196	45.64301	-121.937449	Secondary Contingency Location
197	45.643084	-121.937382	Secondary Contingency Location
198	45.643009	-121.937296	Secondary Contingency Location
Sample Number	**Latitude**	**Longitude**	**Sample Type**
199	45.643085	-121.937227	Secondary Contingency Location
200	45.643007	-121.937141	Secondary Contingency Location
201	45.643084	-121.937084	Secondary Contingency Location
202	45.643008	-121.936994	Secondary Contingency Location
203	45.643085	-121.936931	Secondary Contingency Location
204	45.643009	-121.936834	Secondary Contingency Location
205	45.643079	-121.936762	Secondary Contingency Location
206	45.643011	-121.936679	Secondary Contingency Location
207	45.64308	-121.936616	Secondary Contingency Location
208	45.643003	-121.936533	Secondary Contingency Location
209	45.643072	-121.936468	Secondary Contingency Location
210	45.643244	-121.936435	Primary Contingecy Location
211	45.64316	-121.936378	Primary Contingecy Location
212	45.643246	-121.936305	Primary Contingecy Location
213	45.643241	-121.936154	Primary Contingecy Location
214	45.643161	-121.936235	Primary Contingecy Location
215	45.643076	-121.936313	Primary Contingecy Location
216	45.64301	-121.936386	Primary Contingecy Location
217	45.643013	-121.936233	Primary Contingecy Location
218	45.643082	-121.936155	Primary Contingecy Location
219	45.64316	-121.936082	Primary Contingecy Location
220	45.643243	-121.93601	Primary Contingecy Location
221	45.643249	-121.935876	Primary Contingecy Location
222	45.643159	-121.935934	Primary Contingecy Location
223	45.643081	-121.935975	Primary Contingecy Location
224	45.643024	-121.936073	Primary Contingecy Location
225	45.643063	-121.935878	Primary Contingecy Location
226	45.643156	-121.935832	Primary Contingecy Location
227	45.643244	-121.935761	Primary Contingecy Location
228	45.643239	-121.935627	Primary Contingecy Location
229	45.643152	-121.935696	Primary Contingecy Location
230	45.643068	-121.935773	Primary Contingecy Location
231	45.643062	-121.935676	Primary Contingecy Location
232	45.64316	-121.935567	Primary Contingecy Location
233	45.643235	-121.935501	Primary Contingecy Location
234	45.64323	-121.935375	Primary Contingecy Location
235	45.643152	-121.935459	Primary Contingecy Location
236	45.643061	-121.93556	Primary Contingecy Location
237	45.643068	-121.935446	Primary Contingecy Location
238	45.643073	-121.935334	Primary Contingecy Location

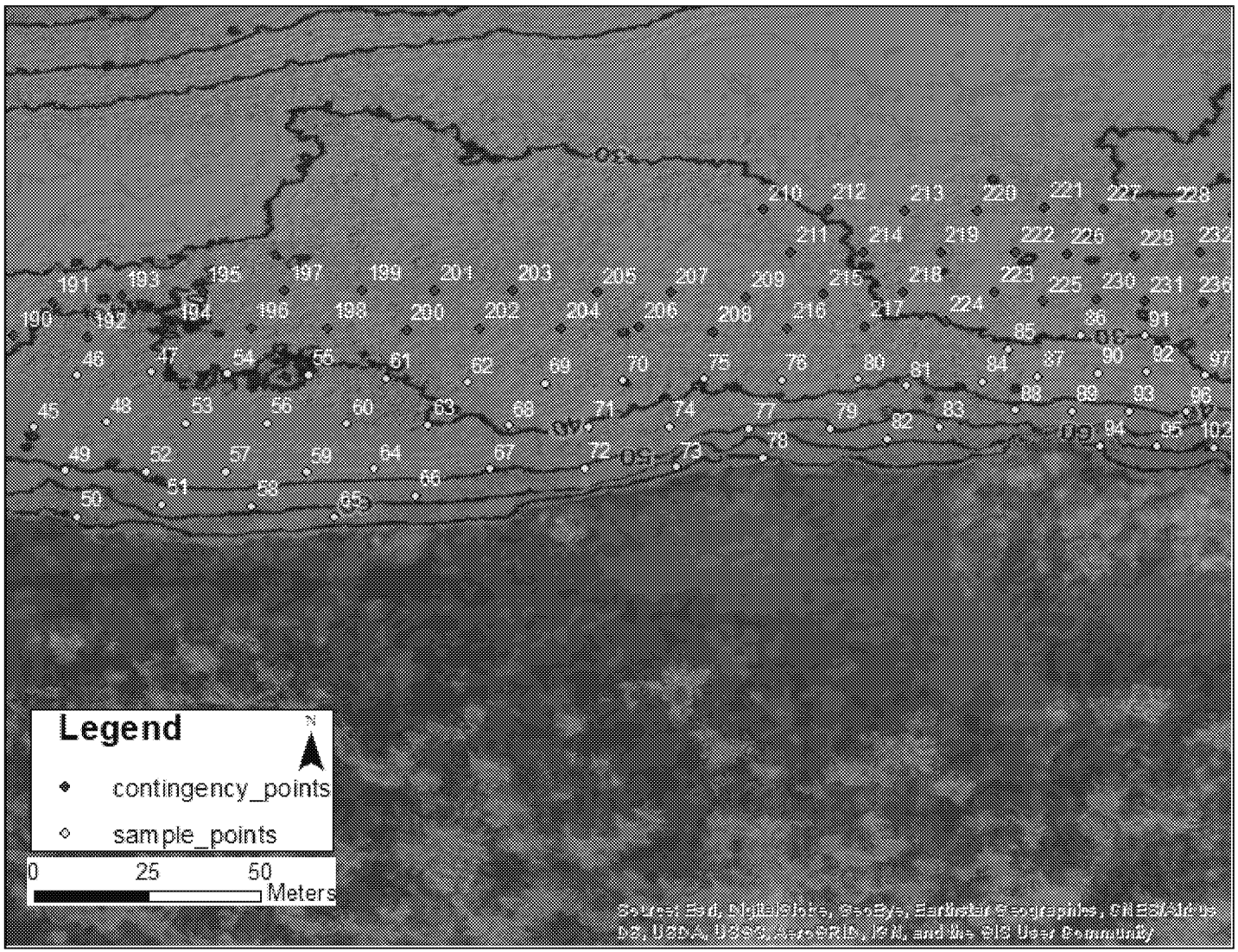
239	45.643159	-121.935316	Primary Contingecy Location
240	45.643236	-121.935255	Primary Contingecy Location
241	45.643172	-121.935205	Primary Contingecy Location
242	45.643063	-121.935237	Primary Contingecy Location
243	45.643057	-121.935122	Primary Contingecy Location
244	45.643173	-121.935087	Primary Contingecy Location
Sample Number	**Latitude**	**Longitude**	**Sample Type**
245	45.643242	-121.93513	Primary Contingecy Location
246	45.643242	-121.935005	Primary Contingecy Location
247	45.643167	-121.934973	Primary Contingecy Location
248	45.643233	-121.934886	Primary Contingecy Location
249	45.643061	-121.935004	Primary Contingecy Location
250	45.643062	-121.934885	Primary Contingecy Location
251	45.643068	-121.934764	Secondary Contingency Location
252	45.642996	-121.934726	Secondary Contingency Location
253	45.643064	-121.934652	Secondary Contingency Location
254	45.642992	-121.9346	Secondary Contingency Location
255	45.643063	-121.934534	Secondary Contingency Location
256	45.642991	-121.934479	Secondary Contingency Location
257	45.643079	-121.934416	Secondary Contingency Location
258	45.642994	-121.934354	Secondary Contingency Location

Appendix C

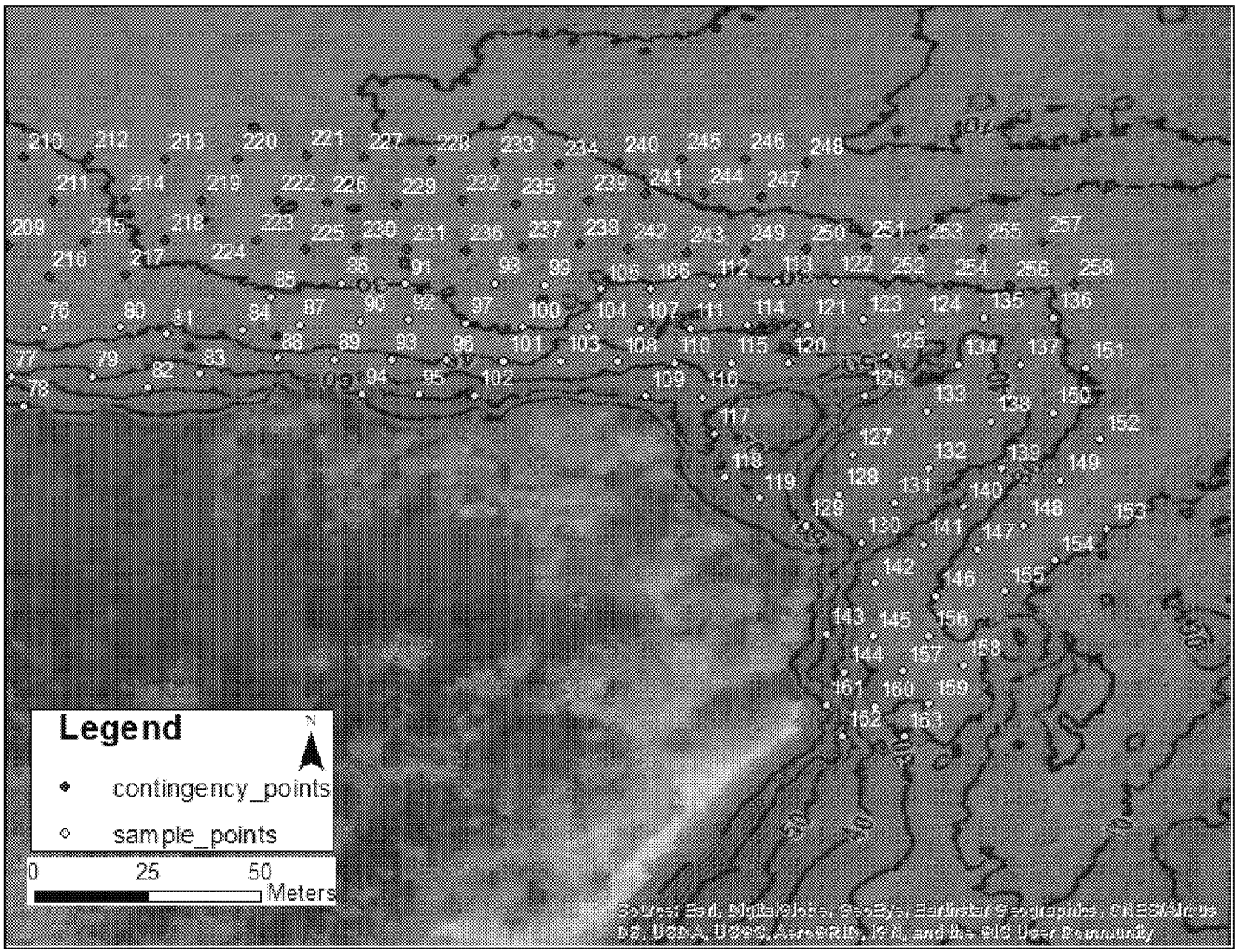
Bradford Island Sampling Location



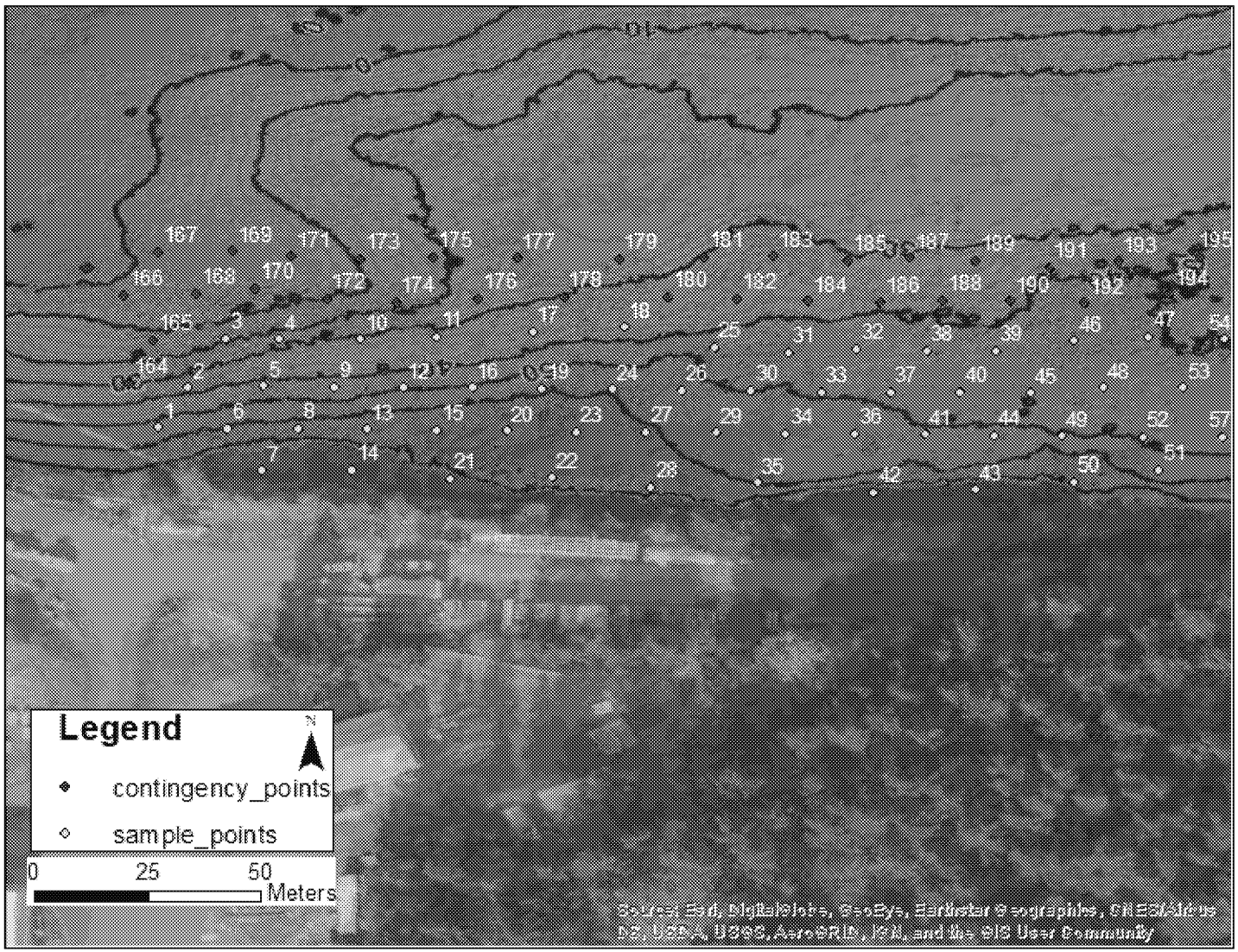
Bradford Island Sampling Location- Central



Bradford Island Sampling Location- East



Bradford Island Sampling Location- West



Appendix D

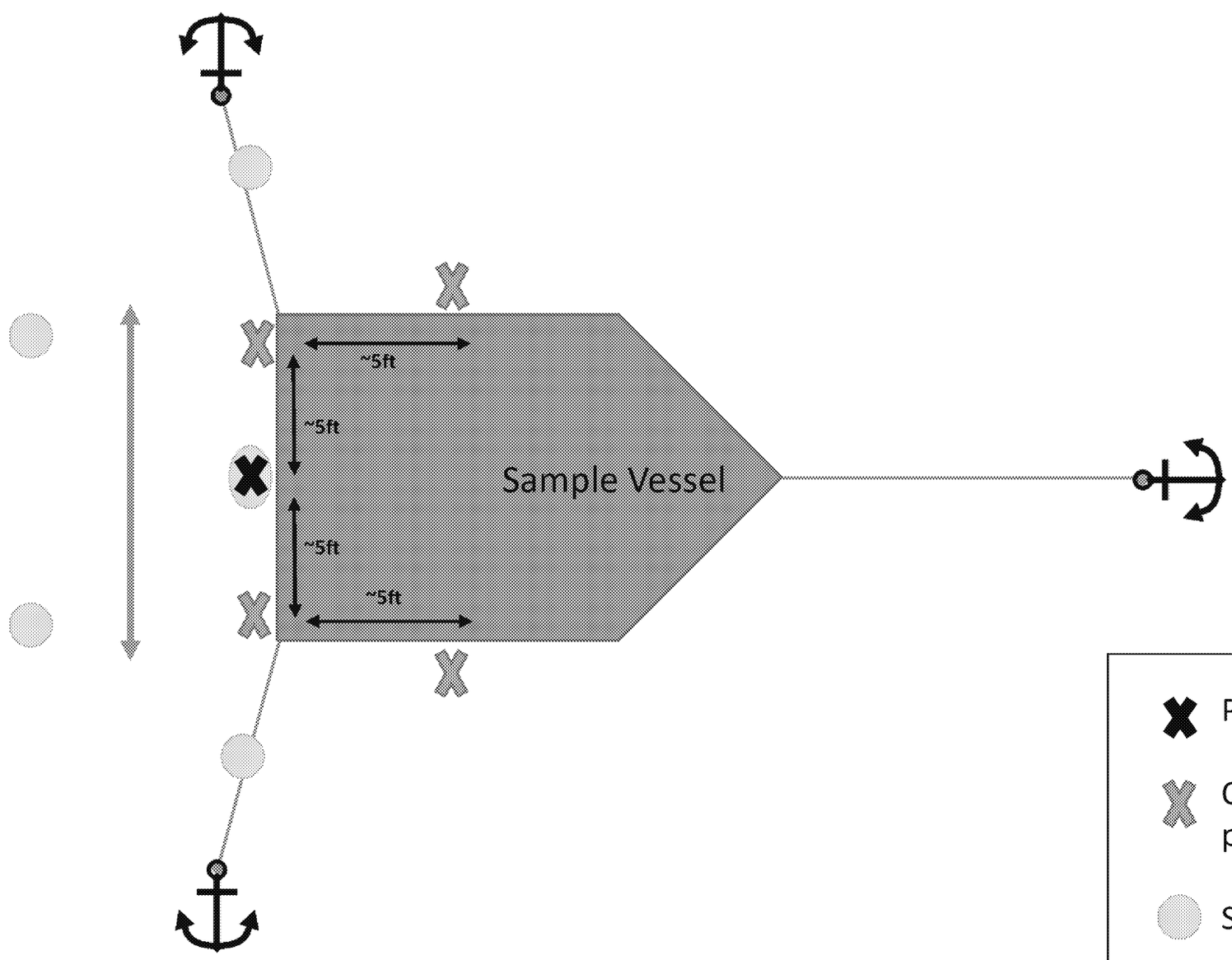
Field Form (to be completed by USACE staff)
Project: Bradford Island River OU Passive Sampling
Date: _____
Field Staff: _____
Field Conditions: _____

SAMPLE ID	HOBO SERIAL #	TIME DEPLOYED/RETRIEVED	LATITUDE	LONGITUDE	WATER DEPTH	NOTES (flow, velocity, etc.)

PAGE #:_____

Appendix E

Appendix E. Vessel Positioning, Sampler Schematic, Sampler Prototype Photos



NOTE: Three point anchoring will only be used in the event that dynamic positioning cannot adequately maintain positioning.

Appendix E. Vessel Positioning, Sampler Schematic, Sampler Prototype Photos

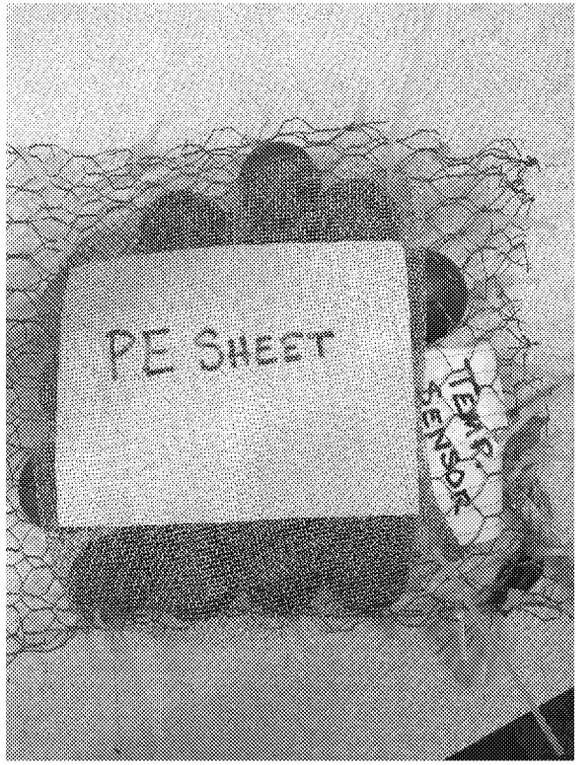


Photo 1. Underside of conceptual prototype with PE sheet secured in mesh envelope and affixed to weighted bag with zip ties.

Photo 2. Side view of conceptual prototype with 1.5-2" steel balls secured in wire pouch.

Photo 3. Top view of conceptual prototype with caribeener attached to top of weighted bag with rope line.

Appendix F

ACTIVITY HAZARDS ANALYSIS

Overall Risk Assessment Code (RAC) (Use highest code): M

Date: 27 January 2020 Project: The Bonneville Dam

Activity: Redlinger Sampling Placing Deployment (27JAN20-05FEB20)

Activity Location: Upper Northern Bradford Island Inner Spillway BRZ

Prepared By: Jesse Allen CENWP-OD-NWH

Risk Assessment Code Matrix

E = Extremely High Risk
H = High Risk
M = Moderate Risk
L = Low Risk

Severity	Probability: Frequent	Likely	Occasional	Seldom	Unlikely
Catastrophic	E	E	H	H	M
Critical	E	H	H	M	L
Marginal	H	M	M	L	L
Negligible	M	L	L	L	L

Add Identified Hazards

	JOB STEPS	HAZARDS	ACTIONS TO ELIMINATE OR MINIMIZE HAZARDS	RAC
X	Work site mobilization and demobilization	Vehicle accident	Safe driving and operating practices will be followed by all personnel. The Bonneville Dam and Cascade Locks Marina are public facilities with high tourist activity and marine traffic All posted speed limits will be strictly followed and extra care shall be taken around crosswalks, blind corners, and docks.	L
X	Safety Brief	Inadequate understanding of health and safety requirements or poor coordination of critical activities	A pre-work safety meeting shall be held prior to operations, detailing the duties and responsibilities of all personnel in the event of an emergency and the location of all emergency equipment by a qualified member of the crew. The meeting will review the Work Plan , review tag out procedures and other procedures related to the The Bonneville Dam Boating Restricted Zone (BRZ) policy. Any questions or concerns regarding the Work Plan and BRZ shall be addressed at this time, if not prior.	L

ACTIVITY HAZARDS ANALYSIS

	JOB STEPS	HAZARDS	ACTIONS TO ELIMINATE OR MINIMIZE HAZARDS	RAC
X	Vessel Inspection	Inadequate Vessel Preperation	The vessel is tested and inspected to determine safe operations status by experienced personnel completing the following checks: 1. Navigation lights, radar systems, radios, depth sounders, and other navigationally significant equipment shall be inspected to ensure proper operation. 2. Inspect for water tight integrity of the vessel (i.e. hull plug, leaks, and bilges). 3. Maintain load line for stability. 4. Inspect engine compartment for leaks. It contains blowers and it is properly vented. 5. Check fuel levels and confirm adequate fuel levels for operations. Smoking is prohibited while fueling at all times. Sorbent pads shall be available in the event of a fuel spill. 6. Properly test auxiliary motor and check fuel level. 7. Inspect bilge pump operation. 8. All gear shall be properly secured prior to casting lines. 9. Inspect throw-able flotation device is readily available. 10. Confirm that there is a serviceable life jacket for each person on board vessel. 11. Perform VHF radio check.	L
X	Vessel Operations	Not maintaining a proper watch	Safe Operations include but are not limited to maintaining a weather watch, implementing personal protective equipment, maintaining vessel water tight integrity, vessel inspection, maintaining auxiliary motors, rescue boats or life-saving skiffs, a-frame and winch operations, and proper deck safety. Emergency procedures include but are not limited to deck safety, fire prevention, radio procedures, recovery during man over board or capsizing, exposure, first aid/CPR, completing and submitting a float plan, spill response, collision and grounding. -Lifejackets shall be worn when outside the cabin and at ALL TIMES when operating within the BRZ. -Keep a lookout for other vessels and floating debris. -Give way to all vessels as most recreational users do not know the "rules of the road". - Keep in contact with commercial traffic, monitor channels 16 at all times; listen to all "Notice to Mariners" broadcasts. Monitor channel 13 for commercial traffic or ship to ship and bridges; channel 14 for dam and lock operations. -In a swift current be extremely cautious, if the vessel loses power or steering the vessel could flip or become flooded with water when it comes arrest on an object. - Watch out for ropes that could be attached to piling when on the downstream side, as rope could get caught in the jet pump intake or propellers. -When operating near the dam be aware of turbulent waters , strong back eddies and avian wire clearance.	L

ACTIVITY HAZARDS ANALYSIS

	JOB STEPS	HAZARDS	ACTIONS TO ELIMINATE OR MINIMIZE HAZARDS	RAC
X	Vessel Operations	Person overboard	In the event of a person overboard, assign one crew member to deploy life ring and maintain eye contact with the victim while the vessel operator maneuvers for pick up. Deploy life sling and circle victim with pickup line for retrieval on stern platform. Do not tow victim and do stop engine prior to pulling victim near jet drive or prop. Be aware of the sea state and current as victim approaches stern.	L
X	Vessel Operations	Exposure	Personnel are responsible to wear appropriate clothing for the daily operations. Cold or heat exposure may occur in or out of the water. In the event of cold shock, hypothermia, heat stress, or heat stroke operations will cease and the victim will be brought to medical assistance. Warming blankets will on-board vessel in cold weather.	M
X	Vessel Operations	Operation of Vessels near Locks and Dams	When operating in the Boat Restricted Zone (BRZ), procedures established in the USACE The Bonneville Lock and Dam Boat Restricted Zone Policy shall be followed. The first AP to encounter the hazard shall verify the outage by coordinating with the OPERATIONS office to ensure the spillway gates do not operate Crews shall maintain contact with the control room on VHF Channel 14 and keep them informed on operations. Permission shall be obtained from the control room before entering restricted areas and inform the control room when leaving. Safe clearance forms will be held by qualified project personnel. All crew members shall sign into clearance forms immediately prior to entering and immediately after leaving any areas covered by the clearance. Be aware of lock operations and discharge from locks when operating below dams. Watch for clearance under avian wires when operating in the stilling basin. Coordinate operations with the designated safety boat if required. Maintain regular contact between vessels and have towing lines rigged and ready to deploy. Hard hats and steel toed footwear shall be worn by personnel while working in required areas on the dam.	M

ACTIVITY HAZARDS ANALYSIS

	JOB STEPS	HAZARDS	ACTIONS TO ELIMINATE OR MINIMIZE HAZARDS	RAC
X	Boat Sampling Deployment Operations	Natural hazards	All affected personnel are trained in the recognition and avoidance of natural hazards. Natural hazards include but are not limited to adverse weather conditions. The following guidelines should be used when working in areas or under conditions where natural hazards exist. Before field work warnings of impending severe weather is monitored and relayed to staff. Appropriate precautions are taken to protect personnel and property from the elements if work commences. The Field Lead is responsible for determining the need to terminate or postpone the day's activities. All boat deploying personnel are expected to use good judgment in self protection against the elements, including bad weather conditions and difficult water operating conditions. Watch footing when walking on wet /icy decks wearing work boots in good condition and properly laced. Do not try to carry too much equipment at one time. Make more trips if necessary; if possible maintain three points of contact when stepping on/off boat from all docks and other slippery surfaces.	M
X	Boat Sampling Deployment Operations	Physical hazards	All boat deploying personnel need to exercise extreme caution and maximum awareness while navigating to placement areas, readying equipment and materials, and actually deploying/retrieving gear over board. To assure proper Inner personnel communication and a safe working environment on-board the boat, a designated Crew Member will perform Deck Safety watch duties. via radio. These duties will allow a continuous safety situational awareness between deck operations and the boat operator at all times. In order to prevent possible injury while lifting and handling heavy gear and equipment, workers need to lift heavy items utilizing team work. This team work principle is very important while working over the side and loading/unloading the boat due to shifting load potential.	M

Add Items

	EQUIPMENT	TRAINING	INSPECTION
X	60' aluminum survey vessel Redlinger (twin 825hp)	TBD	TBD

ACTIVITY HAZARDS ANALYSIS

Involved Personnel:

Douglas Bravo, Jesse Allen, Joseph Huskey and Bill Stillwell: CENWP-OD-NWH

William Gardiner, Kristen Kerns, Daniel Carlson, Katie Richwine, Alex Smith, Alison Suess and Jake Williams: CENWS

Alex Barajas

Acceptance Authority (digital signature): STEWART.ALLEN.L.JR.1177772859 Digitally signed by STEWART.ALLEN.L.JR.1177772859 Date: 2020.01.16 13:58:28 -08'00'

ACTIVITY HAZARDS ANALYSIS

Overall Risk Assessment Code (RAC) (Use highest code): M

Date: 21 November 2019 Project: Bradford Island River OU

Activity: Passive Sampling

Activity Location: Bonneville Dam, Cascade Locks, Oregon

Operation:

Prepared By: Kristen Kerns

Risk Assessment Code Matrix

E = Extremely High Risk
H = High Risk
M = Moderate Risk
L = Low Risk

Severity	Probability				
	Frequent	Likely	Occasional	Seldom	Unlikely
Catastrophic	E	E	H	H	M
Critical	E	H	H	M	L
Marginal	H	M	M	L	L
Negligible	M	L	L	L	L

Add Identified Hazards

JOB STEPS	HAZARDS	ACTIONS TO ELIMINATE OR MINIMIZE HAZARDS	RAC
Travel to/from site.	Traffic accidents; vehicle breakdown; fatigue	Drive defensively, obey traffic laws, drivers to complete mandatory defensive driver training, get sufficient rest before driving/take breaks.	L
Prepare sampling equipment, sampling site access and setup.	Slips, trips, and falls; back strain; hand injuries; pinch points	Be aware of surroundings. Give self enough time to complete tasks. Team lift heavy, large, or awkward items. Use legs to lift - not back. Wear leather gloves when lifting or moving heavy objects. Keep hands and feet clear of heavy objects being lowered to ground surface. All personnel must wear PFD.	L
Deployment and retrieval of passive samplers	Cold water contact, drowning, slips, trips, and falls; back strain - muscle strain;cold stress; hypothermia; precipitation; biological hazards; lighting - visibility.	Remain alert for work site hazards. 3 points of contact when moving around boat. BRZ permit, coordination with dam control room, and current HECP training when entering forebay. Use buddy system - no personnel permitted to work alone. Use sampling tools designed to minimize back/muscle strain during work. Wear clothing appropriate for cold weather and work tasks (Level D). Wear appropriate PPE to include Nitrile gloves, steel toed boots, and eye protection. No eating, drinking, etc. while collecting samples. Inspect work sites for biological hazards before starting work. Only perform work during daylight hours. Follow Site Specific H&S Plan for Bonneville Dam. In event of emergency, radio control room (do not call 911).	M
Decontamination of equipment and PPE.	Slips, trips, and falls	Use buddy system. Give self enough time to decontaminate PPE and equipment. Consider using disposable PPE or equipment for difficult to decontaminate items. Wear appropriate PPE and use good technique when removing PPE. Properly dispose of used/soiled waste materials.	L

Add Items

ACTIVITY HAZARDS ANALYSIS

Add Items

EQUIPMENT	TRAINING	INSPECTION
Add Items		
Add Items		
Add Items		
Add Items		
Add Items		
Add Items		
Add Items		
Add Items		
Add Items		
Add Items		

EQUIPMENT	TRAINING	INSPECTION
EQUIPMENT	TRAINING	INSPECTION
EQUIPMENT	TRAINING	INSPECTION
EQUIPMENT	TRAINING	INSPECTION
EQUIPMENT	TRAINING	INSPECTION
EQUIPMENT	TRAINING	INSPECTION
EQUIPMENT	TRAINING	INSPECTION
EQUIPMENT	TRAINING	INSPECTION
EQUIPMENT	TRAINING	INSPECTION
EQUIPMENT	TRAINING	INSPECTION
EQUIPMENT	TRAINING	INSPECTION

ACTIVITY HAZARDS ANALYSIS

Add Items

	EQUIPMENT	TRAINING	INSPECTION
	EQUIPMENT	TRAINING	INSPECTION
	Sample collection equipment.	Daily tailgate meeting. Current HAZWOPR 8 hr. refresher.	Inspection of equipment prior to use.
	First Aid kit.	Current first aid/CPR training for at least one person (Kristen Kerns, Field Lead) on sampling team.	Inspect first aid kit monthly.
	Personal Flotation Device (PFD)	All staff will be supplied with a PFD from the safety office	daily inspection
	CB Radio	Boat will be equipped with radio and in direct communication with Bonneville Dam Control Room	Daily inspection by boat captain to maintain good working order
	Hazardous Control Energy Program Certification	All staff will complete mandatory online HECP training	Daily lockout-tagout procedures

Involved Personnel:

Kristen Kerns, Bill Gardiner, Dan Carlson, Katie Richwine, Alison Suess, Jake Williams, Bonneville Dam Project Staff, Texas Technical University contract staff

Approval Authority (Type): Collateral Duty Saftey Officer

Approval Authority (Signature): MARSH.JOSEPH.R.1201777662